Thermal Decomposition and Autoxidation of Cobalt Acetylacetonates

By **G. Vasvári, I. P. Hajdu, and D. Gál,*** Central Research Institute for Chemistry, Budapest, Hungary

The thermal decomposition and oxidation of $Co(acac)_3$ and $Co(acac)_2$ have been investigated. It was established that in the absence of oxygen between 100 and 130 °C $Co(acac)_3$ was reduced to $Co(acac)_2$, while $Co(acac)_2$ did not undergo decomposition under similar conditions. The corresponding rate constants and activation energies were determined. Both $Co(acac)_3$ and $Co(acac)_2$ are oxidized stepwise to $Co(OAc)_2.xH_2O$ in the presence of oxygen. The intermediate of the oxidation process is presumably $Co(acac)(OAc)_2$. It was experimentally proved that $RO_2^{\bullet}$-type radicals generated in the system can interact with both acetylacetonates. The rate constant of the interaction between peroxy-radicals and $Co(acac)_3$ has been calculated. Mechanisms for both the decomposition and oxidation reactions have been suggested.

ACETYLACETONATES of transition metals, *e.g.*, cobalt acetylacetonates, are excellent homogeneous catalysts in the liquid-phase oxidation of hydrocarbons. In order to obtain the detailed mechanism of such processes, the kinetics of the overall catalytic reactions have been investigated.[1-5]

Since in these processes the catalysts themselves undergo chemical changes, it seemed expedient to study their decomposition and autoxidation in the absence of the parent hydrocarbons, in inert solvents.

The thermal decomposition and oxidation of cobalt acetylacetonates and their interactions with peroxy-radicals in chlorobenzene were studied in order to find an answer to the question: how much these reactions are to be taken into account in the interpretation of the catalytic effect.

Such processes were recently studied both in polar and non-polar solvents by several authors, using different metal acetylacetonates. During thermal decomposition in an inert atmosphere transition-metal complexes of acetylacetonates were found to yield acetone and carbon dioxide,[6,7] while their autoxidation in non-polar solvents resulted in the reduction of the central metal atoms of higher valency state, accompanied by simultaneous oxidation of the ligand.[8-11] Oxidation was essentially similar in polar solvents.[12,13] The present paper deals with the thermal decomposition and autoxidation of Co^{III} and Co^{II} acetylacetonate complexes.

EXPERIMENTAL

Materials.—Reagent grade chlorobenzene was shaken with aqueous $NaHSO_3$ (10%), separated, dried ($CaCl_2$), and distilled. The solvent obtained (free from benzaldehyde) was used as inert solvent.

Cobalt(III) acetylacetonate, $Co(acac)_3$, was prepared and purified by the method of Bryant and Fernelius[14] (Found: C, 50·8; H, 6·0. Calc. for $C_{15}H_{21}CoO_6$: C, 50·57; H, 5·97%).

Cobalt(II) acetylacetonate, $Co(acac)_2$, was synthesised as described by Ellern and Ragsdale.[15] Purity was checked by i.r. spectra (no trace of Co^{III} complex) (Found: C, 45·6; H, 5·65; Co, 18·6. Calc. for $C_{10}H_{14}CoO_4$: C, 46·7; H, 5·45; Co, 22·6%). [Co was determined by backweighing and it is likely that the loss of Co is due to the sublimation of $Co(acac)_2$.]

Procedure.—Experiments were carried out in a silicone-coated glass vessel provided with a reflux condenser. The gases (oxygen or argon) were introduced through a capillary tube at the bottom of the reaction vessel and samples were taken through a side arm provided with a stopcock. Stirring was by the bubbling gas. For the kinetic runs chlorobenzene (30—50 cm^3) was placed in the reaction vessel which was immersed in a thermostat. The gas bubbling was already started in the warm-up time and the cobalt complex was added to the solvent after thermal equilibrium was reached. The flow rate of oxygen in the autoxidation runs was varied in the range 6—18 l h^{-1} to ensure saturation and in the thermal decompositions argon was bubbled through the liquid.

Analysis.—The changes in the valency state of the catalysts were followed spectrophotometrically by use of a Spectromom 401 instrument. Two versions of the analysis were applied.

(*A*) 3·5 cm^3 of the sample was centrifuged to separate the precipitate (if any) from the liquid. The precipitate, which proved to be Co^{II} acetate, $Co(OAc)_2$, as reported previously[16] was washed with benzene, dissolved in aqueous 1M-NH_4SCN (1 cm^3) and after the addition of acetone (2 cm^3) the absorption of the resulting blue solution was measured at 620 nm (ε 1740). The $Co(acac)_3$ content of the green supernatant liquid was measured directly at 620 nm (ε 113). For the determination of the $Co(acac)_2$,

---

[1] P. George, E. Rideal, and A. Robertson, *Proc. Roy. Soc.*, 1946, *A*, **185**, 283.

[2] N. Ota and T. Tesuka, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1954, **57**, 641.

[3] J. Wibaut and A. Strong, *Proc. k. ned. Akad. Wetenschap.*, 1951, **54**, *B*, 102.

[4] I. Kamiya and K. U. Ingold, *Canad. J. Chem.*, 1964, **42**, 1027.

[5] N. M. Emanuel, I. T. Denisov, and Z. K. Maizus, 'Chain Reactions of Hydrocarbon Oxidation in Liquid Phase,' Nauka, Moscow, 1969 (in Russian).

[6] R. G. Charles, W. M. Hickam, and M. A. Pawlikowsky, *J. Phys. Chem.*, 1958, **62**, 440.

[7] R. G. Charles, W. M. Hickam, and M. A. Pawlikowsky, *J. Phys. Chem.*, 1958, **62**, 1098.

[8] M. A. Mendelsohn, E. M. Arnett, and H. Freiser, *J. Phys. Chem.*, 1960, **64**, 660.

[9] E. M. Arnett, H. Freiser, and M. A. Mendelsohn, *J. Amer. Chem. Soc.*, 1962, **84**, 2482.

[10] E. M. Arnett and M. A. Mendelsohn, *J. Amer. Chem. Soc.*, 1962, **84**, 3821.

[11] E. M. Arnett and M. A. Mendelsohn, *J. Amer. Chem. Soc.*, 1962, **84**, 3824.

[12] D. Banerjea and S. Dutta Chandhuri, *J. Inorg. Nuclear Chem.*, 1971, **33**, 515.

[13] Tadashi Koga and Tadashi Hara, *Bull. Chem. Soc. Japan*, 1966, **39**, 664.

[14] B. F. Bryant and W. C. Fernelius, *Inorg. Synth.*, 1957, **5**, 188.

[15] J. B. Ellern and R. O. Ragsdale, *Inorg. Synth.*, 1968, **11**, 82.

[16] G. Vasvári, P. Hajdu, I. Kende, and D. Gál, *Magyar Kém Folyóirat*, 1971, **77**, 625.

3 cm^3 of this green solution was extracted three times with aqueous 1M-NH_4SCN (1·2, 1, and 1 cm^3). Each extract was diluted with double the amount of acetone and the absorptions of the blue solutions were measured at 620 nm [since the complex measured is the same as in the case of $Co(OAc)_2$ the value of ε is also the same].

(*B*) $Co(OAc)_2$ was determined according to (*A*). The supernatant liquid was extracted three times with water containing 1% Na_2SO_4 to reduce frothing (1·2, 1, and 1 cm^3), and the absorptions of the combined green extracts were measured directly at 620 nm [$Co(acac)(OAc)_2$, ε 133]. The next step was the reduction of $Co(acac)(OAc)_2$ by one drop of hydrazine hydrate. After adding a mixture of one part of 1M-NH_4SCN and two parts of acetone to the reduced extract we measured the blue solution at 620 nm [$Co(acac)_2$ + reduced $Co(acac)(OAc)_2$]. The organic layer of the extracted supernatant liquid which contained the $Co(acac)_3$ was also measured at 620 nm after drying (Na_2SO_4).

RESULTS

Thermal Decomposition of $Co(acac)_3$.—The experiments were carried out in chlorobenzene under argon. The concentration of the chelate was varied between $3·3 \times 10^{-4}$ and 1×10^{-2}M in the temperature range 100—130 °C.

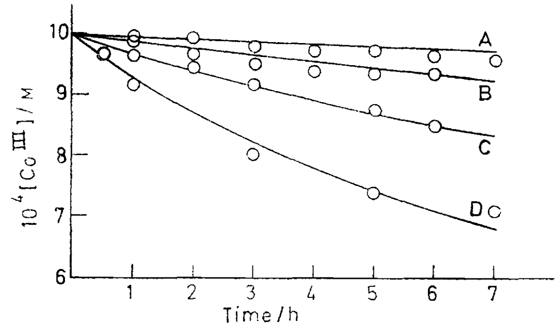
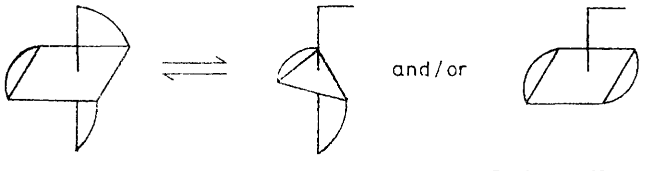


FIGURE 1 Decomposition of $Co(acac)_3$ in chlorobenzene at different temperatures, A, 100 °C; B, 110 °C; C, 120 °C; and D, 130 °C; $[Co(acac)_3]_0 = 1 \times 10^{-3}$M. ——, calculated curves; ○, experimental points

It has been shown that in this temperature region $Co(acac)_3$ absorption decreased with time at a rate increasing with temperature. The initial rate of $Co(acac)_3$ consumption was proportional to its initial concentration. Based on analysis (*A*) it was established that no precipitate was formed during decomposition and the total amount of $Co(acac)_3$ consumed was recovered in the form of $Co(acac)_2$. Transformation never exceeded 50% [in artificial mixtures of $Co(acac)_3$ and $Co(acac)_2$ (1 : 1) no decomposition was observed].

The temperature dependence of transformation is shown in Figure 1.

The experiments pointed to the opening of one chelate ring of the octahedral $Co(acac)_3$ followed by the cleavage of the C–O bond of the ligand, yielding $Co(acac)_2$.



This assumption is strongly supported by the results of Fay *et al.*[17,18] who also supposed short-lived intermediates in the optical inversion and geometrical racemization of $Co(acac)_3$ and related compounds. The $Co(acac)_2$ formed was capable of dimerization with the ' opened-up ' $Co(acac)_3$

This mechanism explains the fact that the reaction is of the first order with respect to $Co(acac)_3$ and that the Co^{III} consumed was recovered as Co^{II}.

The formation of radicals in the decomposition of Co^{III} chelates was proved by Kastning *et al.*[19] in the Co^{III}-initiated polymerization of styrene and ethylene. Thereafter the mechanism (1)—(4) can be assumed for the decomposition process, where $Co(acac)_2acac$ represents the ' opened-up ' chelate and D is the stabilized dimer.

$$Co(acac)_3 \xrightarrow{k_1} Co(acac)_2acac \qquad (1)$$

$$Co(acac)_2acac \xrightarrow{k_{-1}} Co(acac)_3 \qquad (-1)$$

$$Co(acac)_2acac \xrightarrow{k_2} Co(acac)_2 + acac\cdot \qquad (2)$$

$$Co(acac)_2acac + Co(acac)_2 \xrightarrow{k_3} D \qquad (3)$$

$$2\ acac\cdot \xrightarrow{k_4} \text{stable products} \qquad (4)$$

If we consider that the rate-determining step is reaction (2) and apply the steady-state treatment we obtain equations (5) and (6). Using the rate values of our decomposition experiments and the value of k_1 in the literature[17]

$$\frac{d[Co(acac)_3]}{dt} = -\frac{k_1}{1 + k_{-1}/2k_2}[Co(acac)_3] \qquad (5)$$

$$\frac{d[D]}{dt} = \frac{k_1[Co(acac)_3]}{2(1 + k_{-1}/2k_2)} \qquad (6)$$

we found that $36 \leqslant k_{-1}/2k_2 \leqslant 81$, depending on the temperature and so 1 can be neglected in the denominator of equations (5) and (6). After integration of the corresponding differential equations we obtain (7). The absorption

$$[D] = \frac{[Co(acac)_3]_0}{2}\left[1 - \exp\left(-\frac{2k_1k_2}{k_{-1}}t\right)\right] \qquad (7)$$

measured during the reaction, if we neglect the absorption caused by the $Co(acac)_2$ at 620 nm, is due to the ' free ' $Co(acac)_3$ as well as to the $Co(acac)_3$ in dimeric form [equation (8)].

$$[Co(acac)_3]_{exp} = \frac{[Co(acac)_3]_0}{2}\left[1 + \exp\left(-\frac{2k_1k_2}{k_{-1}}t\right)\right] \qquad (8)$$

The activation energy of the overall decomposition reaction is 26 kcal mol^{-1} and the ratio of the rate constants k_{-1} to k_2 is given in equation (9) if we accept equation (10)

$$\frac{k_{-1}}{k_2} = 9·12 \times 10^6 \exp\left(-\frac{8800}{RT}\right) \qquad (9)$$

$$k_1 = 2·4 \times 10^{16} \exp\left(\frac{-34\,800}{RT}\right) \qquad (10)$$

reported by Fay, Girgis, and Klabunde.[17] The calculated

---

[17] R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, 1970, **92**, 7056.

[18] A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, 1970, **92**, 7061.

[19] E. G. Kastning, H. Naarmann, H. Reis, and Ch. Berding, *Angew. Chem.*, 1965, **77**, 315.

decomposition curves at different temperatures are given in Figure 1.

This mechanism is supported by the experiments where the αα'-azobisisobutyronitrile (AIBN) initiator was added to the reaction mixture during thermal decomposition. These runs were carried out at 100 °C where the thermal decomposition of $Co(acac)_3$ was negligible compared with that of the initiator. The decomposition rate of $Co(acac)_3$ remain unchanged, that is, radicals generated from the azobisisobutyronitrile did not induce decomposition.

Thermal Decomposition of $Co(acac)_2$.—Experiments were carried out under the same conditions used for the study of the thermal decomposition of $Co(acac)_3$. In inert solvent and atmosphere no measurable changes could be observed up to 120 °C.

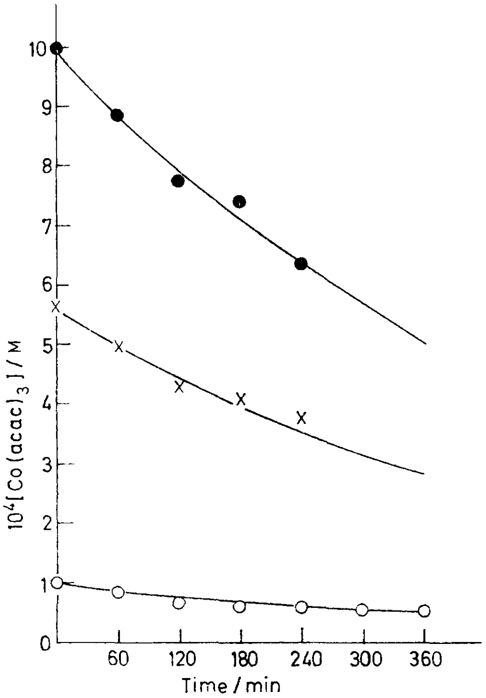


FIGURE 2 Oxidation of $Co(acac)_3$ in chlorobenzene at 120 °C. ——, calculated curve

Autoxidation of $Co(acac)_3$.—Experiments were performed at 100—120 °C and the initial concentration of $Co(acac)_3$ was varied between 1×10^{-4} and 1×10^{-3}M. The flow-rate of oxygen was 6 l h^{-1}.

Varying the chelate concentration and following analysis by version (*A*) we can see the decrease in $Co(acac)_3$ concentration in Figure 2.

A Co^{II} compound [probably $Co(acac)_2$] can be observed in the solution after a certain extent of conversion. The solution becomes turbid owing to the formation of a precipitate, which turned out to be $Co(OAc)_2$. Complete analysis of the system with time is shown in Figure 3. It follows from Figure 3 that $Co(acac)_2$ is an intermediate of the oxidation in the course of which the ligands are oxidized stepwise and the initial $Co(acac)_3$ is reduced to $Co(OAc)_2$. Being insoluble, the hydrate of the latter precipitated. The hydrate water arises from the oxidation of the ligands.[4-7] The initial rate of oxidation is proportional to the initial concentration of $Co(acac)_3$.

In order to obtain the activation energy of oxidation, the logarithm of the initial oxidation rates are plotted against $1/T$ (Figure 4). The Arrhenius dependence is satisfactory,

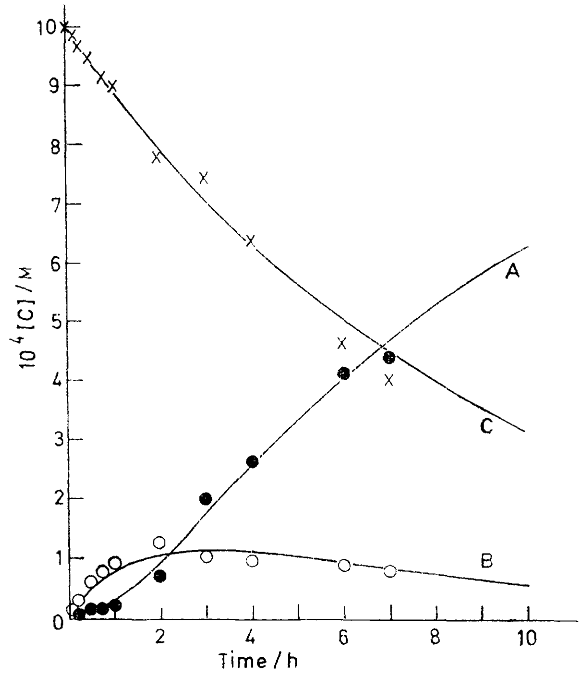


FIGURE 3 Oxidation in chlorobenzene at 120 °C of A, $Co(OAc)_2$; B, $Co(acac)_2$; C, $Co(acac)_3$; ——, calculated curve

although the temperature region studied was rather narrow (20 K) since below 100 °C the reaction was very slow and above 120 °C the loss was too high owing to the low b.p. of the solvent. The activation energy was $E = 46{\cdot}8$ kcal mol^{-1}.

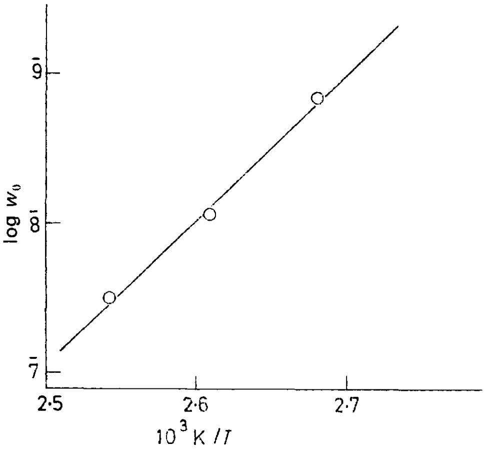


FIGURE 4 The log of the initial rates of the $Co(acac)_3$ oxidation against reciprocal temperature in chlorobenzene; $[Co(acac)_3]_0 = 1 \times 10^{-3}$M

The mechanism (11)—(15) has been assumed for the oxidation. This mechanism represents the sequence of transformation $Co(acac)_3 \longrightarrow Co(acac)_2 \longrightarrow Co(OAc)_2$. The existence of adducts resembling the complex

$Co(acac)_2 \cdots O_2$ has been proved so far only for nitrogen-containing ligands though in oxidations it was assumed earlier.[20,21]

$$Co(acac)_3 + O_2 \xrightarrow{k_{11}} Co(acac)_2 + acacO_2\cdot \qquad (11)$$

$$acacO_2\cdot \xrightarrow[Co(acac)_3]{k_{12}} Co(acac)_2 + (acac)_2O_2 \qquad (12)$$

$$acacO_2\cdot \xrightarrow[acacO_2\cdot]{k_{13}} O_2 + \text{stable products} \qquad (13)$$

$$Co(acac)_2 + O_2 \overset{K_{14}}{\rightleftharpoons} Co(acac)_2 \cdots O_2 \qquad (14)$$

$$Co(acac)_2 \cdots O_2 \xrightarrow{k_{15}} Co(OAc)_2 + \text{stable products} \qquad (15)$$

Since in the oxidations of hydrocarbons peroxy-radicals play an important role their effect exerted on the oxidation of $Co(acac)_3$ has been also investigated. In order to generate peroxy-radicals the azobisisobutyronitrile initiator was used at temperatures where the oxidation rate of the chelate can be neglected compared with the decomposition rate of the initiator. Results are shown in Figure 5, whence it can be established that peroxy-radicals markedly accelerate $Co(acac)_3$ consumption and the formation of both $Co(acac)_2$ and $Co(OAc)_2$.

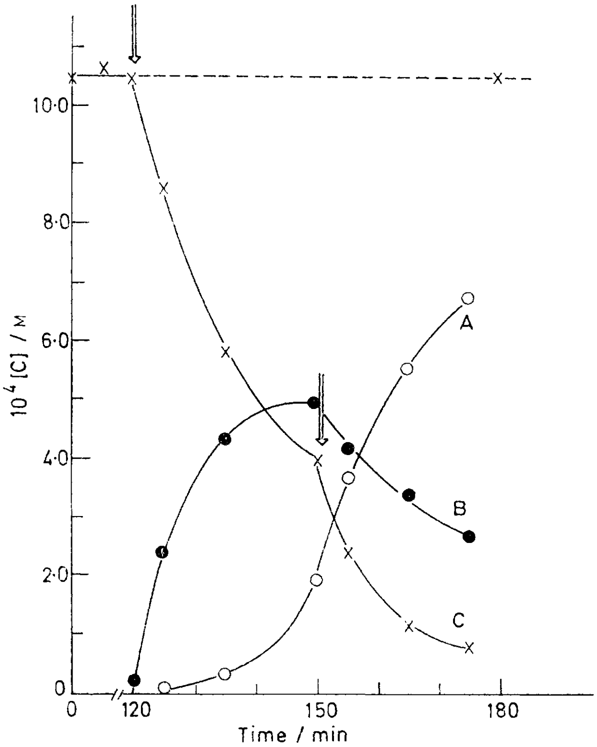


FIGURE 5 Oxidation of $Co(acac)_3$ in chlorobenzene at 100 °C; introduction of azobisisobutyronitrile marked by an arrow; A, $Co(OAc)_2$; B, $Co(acac)_2$; C, $Co(acac)_3$

These experiments support the existence of step (12) according to which peroxy-type radicals are capable of reducing $Co(acac)_3$ to $Co(acac)_2$.

The higher overall oxidation rates of $Co(acac)_3$ compared with its decomposition rates indicate that step (11) is fast compared with (2). Accordingly, the differential equations (16)—(18) can be deduced. If in the initial stages of

$$\frac{d[Co(acac)_3]}{dt} = -k_{11}[Co(acac)_3][O_2] - k_{12}[Co(acac)_3][acacO_2\cdot] \qquad (16)$$

$$\frac{d[Co(acac)_2]}{dt} = k_{11}[Co(acac)_3][O_2] + k_{12}[Co(acac)_3][acacO_2\cdot] - K_{14}k_{15}[Co(acac)_2][O_2] \qquad (17)$$

$$\frac{d[Co(OAc)_2]}{dt} = K_{14}k_{15}[Co(acac)_2][O_2] \qquad (18)$$

oxidation, the consumption of radicals due to recombination is neglected the equations can be reduced to (19)—(21).

$$\frac{d[Co(acac)_3]}{dt} = -2k_{11}[Co(acac)_3][O_2] \qquad (19)$$

$$\frac{d[Co(acac)_2]}{dt} = 2k_{11}[Co(acac)_3][O_2] - K_{14}k_{15}[Co(acac)_2][O_2] \qquad (20)$$

$$\frac{d[Co(OAc)_2]}{dt} = K_{14}k_{15}[Co(acac)_2][O_2] \qquad (21)$$

After integration we obtain equations (22)—(24). From

$$[Co(acac)_3]_t = [Co(acac)_3]_0 \exp(-2k_{11}[O_2]t) \qquad (22)$$

$$[Co(acac)_2]_t = \frac{2k_{11}}{2k_{11} - K_{14}k_{15}} [Co(acac)_3]_0 \{\exp(-K_{14}k_{15}[O_2]t) - \exp(-2k_{11}[O_2]t)\} \qquad (23)$$

$$[Co(OAc)_2]_t = [Co(acac)_3]_0 \left\{1 + \frac{K_{14}k_{15}}{2k_{11} - K_{14}k_{15}} \exp(-2k_{11}[O_2]t) - \frac{2k_{11}}{2k_{11} - K_{14}k_{15}} \exp(-K_{14}k_{15}[O_2]t)\right\} \qquad (24)$$

the values obtained for $k_{11}^{120} = 2{\cdot}08 \times 10^{-3}$ and $(K_{14}k_{15})^{120} = 2{\cdot}54 \times 10^{-2}$ l mol^{-1} s^{-1} the calculated curves of concentrations against reaction time shown in Figures 2 and 3 agree well with the experimental points (solubility of oxygen in chlorobenzene at the temperature of the experiments was taken as $0{\cdot}77 \times 10^{-2}$M).

If the oxidation of the chelate proceeds in oxidizable solvents capable of yielding $RO_2\cdot$-type radicals, depending on the concentration of the latter, reaction (12) and/or (12′) should be taken into account. Naturally when this

$$Co(acac)_3 + RO_2\cdot \xrightarrow{k_{12'}} Co(acac)_2 + ROOacac \qquad (12')$$

occurs reaction (13) and/or reaction (13′) will be the rate-

$$2RO_2\cdot \xrightarrow{k_{13'}} O_2 + \text{stable products} \qquad (13')$$

controlling termination. From Figure 5 it seems very likely that the sudden drop in the concentration of $Co(acac)_3$ after the introduction of azobisisobutyronitrile is the direct consequence of reaction (12′). Therefore an approximate calculation of $k_{12'}$ can be carried out through equations (25)—(27). The following values were used: $e = 0{\cdot}8$;

$$w_i = \frac{d[Co(acac)_3]}{dt} + k_{13'}[RO_2\cdot]^2 \qquad (25)$$

$$\frac{d[Co(acac)_3]}{dt} = k_{12'}[Co(acac)_3][RO_2\cdot] \qquad (26)$$

$$w_i = 2ek_i[AIBN] \qquad (27)$$

---

[20] N. Uri, *Nature*, 1956, **177**, 1177.

[21] E. T. Denisov and N. M. Emanuel, *Zhur. fiz. Khim.*, 1956, **30**, 2499.

$k_i^{120} = 1{\cdot}24 \times 10^{-3}$ s^{-1}; and $k_{13'} = 1{\cdot}6 \times 10^7$ l mol^{-1} s^{-1}. The corresponding value of the rate constant is given by equation (28) at 120 °C.

$$k_{12'} \cong 1 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1} \qquad (28)$$

Autoxidation of Co(acac)$_2$.—The initial concentration of the chelate was varied between 1×10^{-4} and 1×10^{-2}M while the reaction temperature changed between 80 and 120 °C. The flow rate of oxygen was 6—18 l h^{-1} depending on the catalyst concentration.

The originally pink solution became first colourless then green. According to analysis (*A*) Co(acac)$_3$ was formed. The kinetic curves are shown in Figure 6. However, the deficiency of cobalt in the material balance indicates that an unknown compound was formed during the oxidation.

Analysis (*B*) gave the following results: the unknown compound is a water-soluble, greenish material containing Co^{III}. It can oxidize instantly KI in acidic solution to iodine. Its aqueous solution can be reduced with hydrazine hydrate even at low temperatures accompanied by the simultaneous disappearance of its greenish colour. We succeeded in precipitating this compound from the oxidation mixture, but the purity of the solid sample was not satisfactory and it decomposed at room temperature (smelling of acetylacetone). I.r. spectroscopy [22] indicated the presence of Co^{III}, acetylacetone, and acetate anion groups.

Based on the similarity to the compounds reported in the literature [23-29] and because of the lack of the OH group it was assumed that its composition was Co(acac)(OAc)$_2$. In order to prepare such a compound we oxidized Co(OAc)$_2$ in chlorobenzene with H$_2$O$_2$ in the presence of acetylacetone. The i.r. spectrum of the freshly prepared compound was identical with that of the compound precipitated from the oxidation.

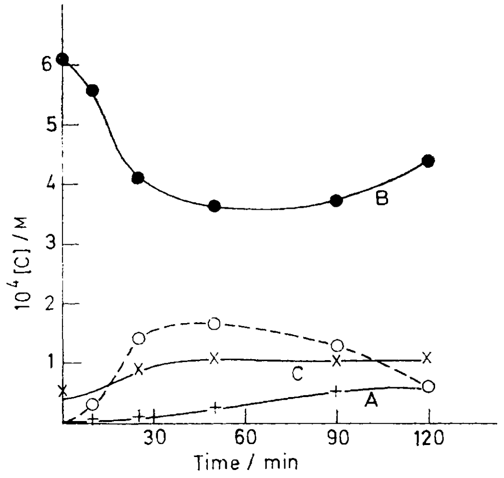


FIGURE 6 Oxidation of Co(acac)$_2$ in chlorobenzene at 100 °C; [Co(acac)$_2$]$_0$ = 6×10^{-4}M; A, Co(OAc)$_2$; B, Co(acac)$_2$; C, Co(acac)$_3$; the broken line represents the deficiency in cobalt

The order of the reaction concerning the consumption of Co(acac)$_2$ has been calculated from the rate maxima and found to be 2 with respect to the initial Co^{II} concentration. The activation energy was 16·5 kcal mol^{-1}.

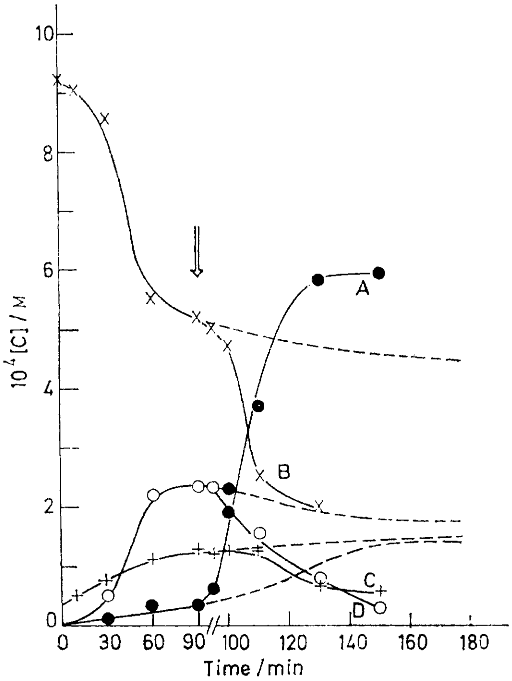


FIGURE 7 Oxidation of Co(acac)$_2$ in chlorobenzene at 80 °C; introduction of azobisisobutyronitrile marked by an arrow; A, Co(OAc)$_2$; B, Co(acac)$_2$; C, Co(acac)$_3$; D, Co(acac)(OAc)$_2$

It should be noted that Co(acac)$_3$ formation could be observed during oxidation and its concentration was proportional to the initial concentration of Co(acac)$_2$.

Peroxy-radicals generated in the system [containing Co(acac)$_2$ and oxygen] yielded curves shown in Figure 7. The radicals were generated at the 90th minute of the reaction introducing azobisisobutyronitrile initiator. From this time on, the decrease in Co(acac)$_2$ concentration was rather steep while the decrease in the concentration of Co(acac)(OAc)$_2$ was less marked. There was no immediate change as might have been expected in the amount of Co(acac)$_3$; later, however, a slight decrease could be observed. It may be assumed that the expected decrease has been compensated by its formation from Co(acac)$_2$ under the influence of the radicals.

DISCUSSION

Our results yield the following picture for the oxidation of Co(acac)$_2$. The ligands of the Co(acac)$_2$ are oxidized stepwise and transformed into Co(OAc)$_2$. The intermediate of the oxidation is presumably Co(acac)(OAc)$_2$.

Taking into account the second order of the oxidation and the corresponding literature evidence,[30-34] we can

---

[22] S. Holly, personal communication.

[23] J. Minczewski and M. Poronicka, *Chem. analit.*, 1964, **9**, 785, 947.

[24] J. Budesinsky, J. Dolezal, B. Sramkova, and J. Zyka, *Microchem. J.*, 1971, **16**, 121.

[25] C. E. Pricker and L. J. Loefler, *Analyt. Chem.*, 1955, **27**, 1419.

[26] J. A. Sharp and A. G. White, *J. Chem. Soc.*, 1952, 110.

[27] E. Koubek and J. O. Edwards, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1401.

[28] R. G. Durrant, *J. Chem. Soc.*, 1905, **87**, 1781.

[29] E. G. V. Percival and W. Wardlaw, *J. Chem. Soc.*, 1929, 2628.

[30] R. G. Wilkins, *Adv. Chem. Ser.*, 1971, **100**, 111.

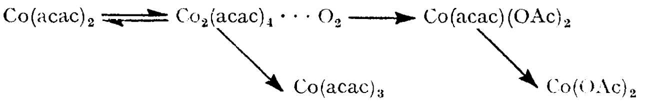
[31] G. L. Goodman, H. G. Hecht, and J. A. Wil, *Adv. Chem. Ser.*, 1962, **36**, 90.

[32] M. Nakai, S. Sato, and Y. Fujimura, *Chubu Kogyo Daigaku Kyo*, 1969, **5**, 151.

[33] Y. Fujimura and T. Mitsui, *Chubu Kogyo Daigaku Kyo*, 1969, **6**, 81.

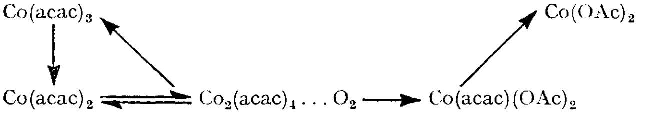
[34] D. Bekoraglu, B. Erdem, and S. Fallab, *Istanbul Univ. FenFak. Mecmussi, Ser. C*, 1964, **29**, 16.

assume the network of Scheme 1. This scheme seems to be consistent with our results; verification would,



SCHEME 1

however, require further experiments. Further it can be applied for the oxidation of $Co(acac)_3$ if completed as in Scheme 2.



SCHEME 2

This means that the compound $Co(acac)(OAc)_2$ assumed should also be formed during the oxidation of $Co(acac)_3$. In order to support this suggestion analysis (*B*) was used for the oxidation of $Co(acac)_3$ giving results shown in Figure 8. The intermediate can be observed, though in small quantity.

This investigation is part of our studies in the field of catalytic oxidation of hydrocarbons. We can now state that the transformation of a catalyst cannot be considered exclusively as interaction with the parent hydrocarbon and its derivatives. Its decomposition and autoxidation could play a role in the course of hydrocarbon oxidation and this role is even more pronounced in their interaction with peroxy-radicals.

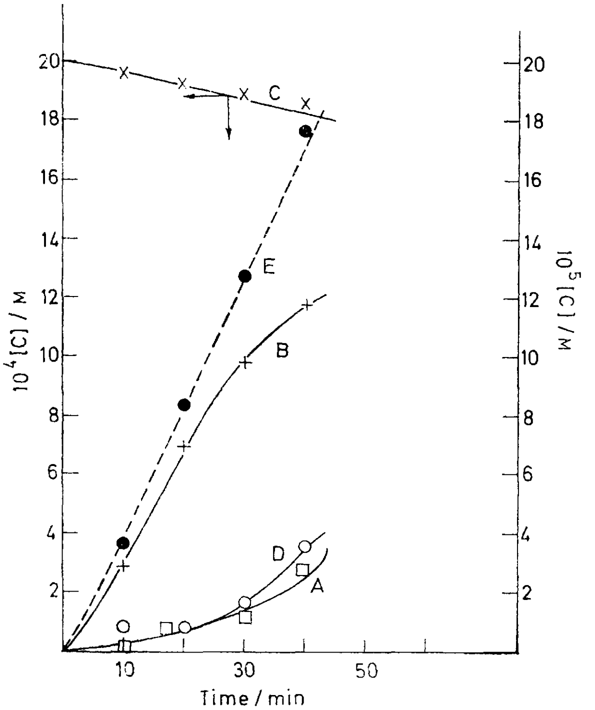


FIGURE 8 Oxidation of $Co(acac)_3$ in chlorobenzene at 120 °C; $[Co(acac)_3]_0 = 20 \times 10^{-4}$ M; A, $Co(OAc)_2$; B, $Co(acac)_2$; C, $Co(acac)_3$; D, $Co(acac)(OAc)_2$; E, $Co(OAc)_2 + Co(acac)_2 + Co(acac)(OAc)_2$

We thank Dr. L. Simándy for discussions and Dr. S. Holly for help with i.r. spectra.

[3/342 *Received*, 14*th February*, 1973]