

THE ROLE OF METAL COMPOUNDS IN THE DEGRADATION OF POLYMERS

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ABSTRACT

The degradation of polymers induced by the presence of metal compounds is a complicated reaction. That is why the reactions of low molecular model compounds have been chosen for systematic studies. The extent of present knowledge about the reactions of metal compounds in non-polar media is so far quite restricted. The metal compounds can act both as the oxidation and reduction agent in the initiation process.

Studies on the oxidation of various substrates with cobalt(III) complexes in the absence of oxygen have revealed that, in some cases, the radicals formed in the first step are either quickly oxidized or recombine.

The course of reaction in an oxygen atmosphere can be substantially influenced by small changes in the structure of the ligands. Moreover, even trace amounts of polar compounds can play an important role. It follows, from the correlation of activation energies with activation entropies, that the reactivity of oxidation agents can be well correlated both for aqueous and for non-polar media. Molecular oxygen fits well in this correlation.

During the reduction initiation, a typical example being the reaction of cobalt(II) with peroxide, complex-bonded radicals are formed in non-polar media. The reactions of these radicals with various polar substrates and other metal-containing compounds have been studied.

INTRODUCTION

It is well known that the degradation of polymers includes many different reactions. It is also known that the only promising way to the elucidation of this complex problem is the separation of individual reactions. That is why we have attempted to study initiation, propagation and termination reactions separately. The reactions have been studied using low-molecular model systems instead of the polymers.

Macromolecular chemistry as a scientific discipline that originated predominantly from organic chemistry, was, until recently, restricted to the study of several elements forming the polymer backbone. The chemistry of coordination compounds was, on the other hand, the domain of inorganic chemistry. This was reflected, e.g. in the description of redox-initiation systems used widely as initiators of radical reactions for several decades.

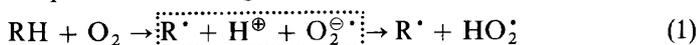
In this particular case only a minimum of attention has been paid to the influence of the ligand attached to the transition metal. It was the discovery of coordination catalysis made by Ziegler which stimulated extensive research in the field of catalytic systems containing transition metals. It was found, however, that catalysts which are suitable for the synthesis of polymers possessing desirable physical properties have, at the same time, a common disadvantage—they are also efficient catalysts of polymer degradation.

Suitable models for degradation studies in polymers can be both linear and cyclic compounds containing the reactive functional groups and their various combinations.

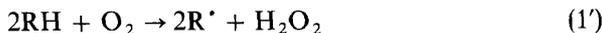
Non-polar media are important for modelling the reaction of metal complexes in polymers. From this point of view present knowledge about reactions of coordination compounds is quite scarce because most of the studies were done using electrochemical methods, i.e. in electrolytically conductive environments. The conditions of experiments were thus substantially different from those under which the reactions take place in polyolefins or in other polymers.

The initiation reaction, i.e. the rate of radical formation, is of primary importance for studies of degradation processes in polymers and consequently for solving the problems connected with the stability of polymers. It is quite obvious that if it were possible to suppress the initiation completely then it would not be necessary to use antioxidants whose function is to deactivate radicals. We are now in a position to decrease the rate of initiation rather than suppress it. This enables us to lower the concentration of antioxidants in a polymer. It follows that antioxidants are an integral part of a polymer system. The study of degradation processes of these additives is thus of the same importance as the studies of degradation of the basic polymer chain.

Let us consider a pure hydrocarbon (i.e. compound that does not contain hydroperoxides) which is in contact with oxygen and a transition metal compound. From the possible mechanisms of the 'primary' initiation reaction let us compare the following two:



Reaction 1 has been studied in some detail by Denisov *et al.*¹ who suggested the trimolecular mechanism, i.e.



It can also be visualized as a consecutive reaction where reaction 3 immediately follows the reaction 1.



Reaction 1 has also been studied by Dulog² and by other authors.

Betts and Uri³ have come to the conclusion that the initiation induced by the presence of metal compounds is of primary importance in all real systems.

It is well known that transition metal compounds can act both as donors and acceptors of electrons in the reaction of initiation of radical reactions.

A typical example of the metal compound acting as an electron donor is the reaction with hydroperoxide



To study the above-mentioned reactions in non-polar media we used cobalt compounds. Cobaltic ions belong to the strongest one-electron oxidizing agents known ($E_0 = +1.84 \text{ V}$ in water) and the structure of cobalt complexes is relatively well understood.

OXIDATION BY Co(III) COMPLEXES

The first attempts to study reaction 2 in a hydrocarbon medium have shown that some substrates yield only one product with a simple stoichiometric ratio of oxidation agent to substrate. Other substrates rendered a mixture of products which signified that different parallel and consecutive reactions respectively had taken place.

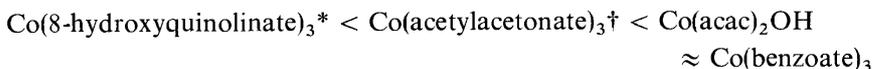
(a) Oxidation of benzylalcohol

Benzylalcohol is an example of a substrate which gave only one product upon oxidation—benzaldehyde. The overall course of reaction can be described as follows:



X being a negatively charged ligand.

The reactivity of the Co(III) complexes examined increases in the following order:



The rate of consumption of the metal complexes during the oxidation of benzylalcohol can be described by various kinetic expressions⁴. e.g.

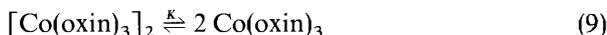
$$-\frac{d[\text{Co(oxin)}_3]}{dt} = k_c[\text{Co(oxin)}_3]^{\frac{1}{2}} \quad (6)$$

$$-\frac{d[\text{Co(benzoate)}_3]}{dt} = k'_c[\text{Co(benzoate)}_3]^{\frac{1}{3}} \quad (7)$$

In both cases the rate-determining step will be the reaction



which in the case of Co(oxin)_3 is preceded by the dissociation of dimers



and in the case of Co(benzoate)_3 by the dissociation of trimer

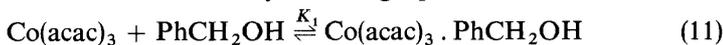


* Denoted as Co(oxin)_3 .

† Denoted as Co(acac)_3 .

As the equilibrium constants K and K' are very low it was possible to determine only the products $k(K^{\frac{1}{2}})$, $k(K'^{\frac{1}{2}})$ and the sums of activation and association energy respectively from the kinetic experimental data.

Since the initial rate of $\text{Co}(\text{acac})_3$ consumption obeys a first order law the reactions of this complex have been studied in some detail. Even in this seemingly simple system there were a series of complications such as: the formation of associates of benzylalcohol itself; most important is the dimerization process; and the formation of a complex between benzylalcohol and $\text{Co}(\text{acac})_3$. The reaction mechanism holding for moderate concentrations of benzylalcohol can be described by following equations:

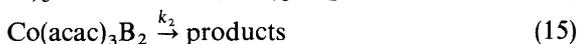
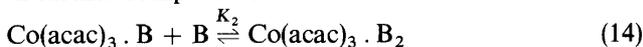


It was found that the equilibrium constant K_1 is affected by the environment

Table 1.

Solvent	$k_1 \times 10^4$ (sec^{-1}) (138°C)	K_1 (l. mol^{-1})
Mesitylene	4.47	2.7
Dichlorobenzene	4.35	2.85
Nitrobenzene	4.4	1.31

whereas k_1 is not, as shown in *Table 1*. At high concentrations of benzylalcohol (B) the addition of another benzylalcohol molecule takes place and the reaction scheme is further complicated:



The $\text{Co}(\text{acac})_2\text{OH}$ disappearance during its reaction with benzylalcohol also follows the first order law even when $\text{Co}(\text{acac})_2\text{OH}$ is present in the form of a dimer.

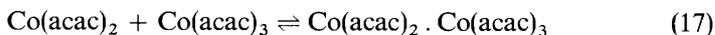
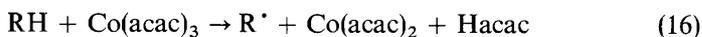
If we are to evaluate the data⁴ critically then the fact that the rate of consumption of oxidizing agent follows a first order law cannot be regarded as evidence that the reacting species is the monomer. Reaction 13 would not be fast if another particle of $\text{Co}(\text{III})$ were not present in the immediate vicinity. That is why it is assumed that the polar oxygen-containing radical $\text{Ph}-\dot{\text{C}}\text{H}-\text{OH}$ reacts more directly in the ligand field of $\text{Co}(\text{III})-\text{Co}(\text{II})$.

(b) Oxidation of hydrocarbons

The first reaction in the case of allylbenzene, cumene and mesitylene oxidation can also be described by reaction 8.

In these cases, i.e. in strictly non-polar media, we have observed that the reaction ceases before the theoretical amounts of components were consumed. It has been proved⁴ that the $\text{Co}(\text{acac})_2$ formed consumes one equivalent of $\text{Co}(\text{acac})_3$ to give an inactive complex $\text{Co}(\text{III}) \cdot \text{Co}(\text{II})$. The

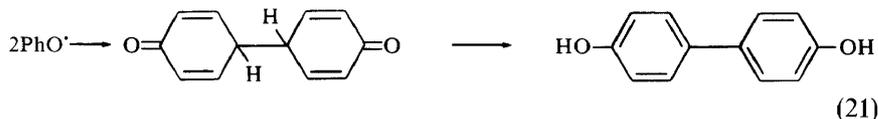
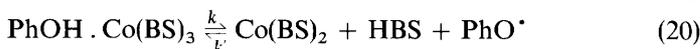
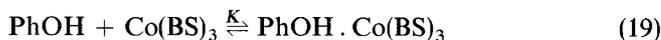
stoichiometric ratio of consumed Co(III):RH is equal to 1.0 to 1.2, i.e. unlike the benzylalcohol case the first formed hydrocarbon radical is not further oxidized. The reaction mechanism can be expressed in the following way:



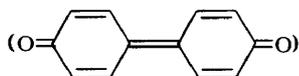
The products of reaction 18 are partially further oxidized.

(c) Oxidation of phenols

The oxidation of phenols by $\text{Co}(\text{acac})_3$ has been examined by Martemjanov and Denisov⁵ who found that the phenol forms a complex with $\text{Co}(\text{acac})_3$ which contains hydrogen bonding. We used both $\text{Co}(\text{N-butyl-salicylaldimine})_3^*$ and $\text{Co}(\text{N-phenyl-salicylaldimine})_3^\dagger$ as oxidation agents for the oxidation of 2,6-dimethylphenol. The following reaction mechanism complies with the results of kinetic experiments and the analysis of products:



The product of reaction 21 is further oxidized to diphenoquinone

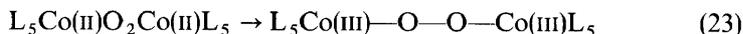
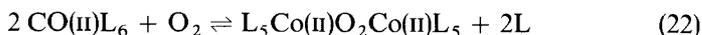


AUTOXIDATION CATALYSED BY Co(II) COMPLEXES

As early as in 1946 Calvin⁷ described several Co(II)-salicylaldimine chelates that could reversibly fix oxygen.

Betts and Uri³ reported that $\text{Co}(\text{BS})_2$ can accelerate the autoxidation of hydrocarbons when present at low concentrations. Higher concentrations of the same compound can, however, act as an inhibitor.

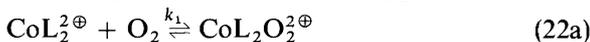
Fallab⁸ has suggested a general reaction mechanism describing the reaction of cobalt complexes with oxygen:



* $\text{Co}(\text{BS})_3$.

† $\text{Co}(\text{PS})_3$.

Wilkins *et al.*⁹ have found that if reaction 22 is carried out in an aqueous medium then the first reaction step is the rate-determining process:



The reaction is then followed by a fast process



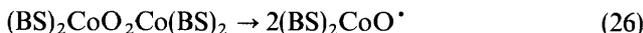
During our experiments we have observed⁶ that reaction 22 does not take place in a strictly non-polar medium and that the presence of electron donors (water, amines) is a necessary condition for this reaction to occur at all. Only a complex such as CoX_2 whose trivalent form is stabilized by electron delocalization from the ligand, can be oxidized by elemental oxygen. For example, the principal difference between $\text{Co}(\text{BS})_2$ and $\text{Co}(\text{PS})_2$ —two very similar compounds—resides in the fact that the latter complex is not oxidizable by oxygen.

Complex $\text{Co}(\text{BS})_2 \cdot \text{O}_2$ and $(\text{BS})_2\text{CoO}_2\text{Co}(\text{BS})_2$, are both very strong oxidation agents. The oxidation of phenol by this complex is a very fast process even at room temperature. The maximum reaction rate is achieved at 30° to 40°C. Part of $\text{Co}(\text{II})$ is slowly irreversibly oxidized to inactive products, whereas in the absence of phenol the irreversible oxidation of $\text{Co}(\text{II})$ takes place at a much higher rate.

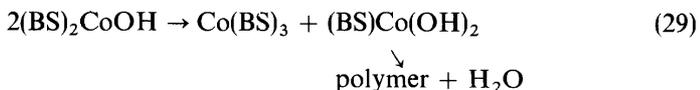
The overall rate of catalysed oxidation can be described by the following expression

$$d[\text{O}_2]/dt = k[\text{Co}(\text{BS})_2]^2 [\text{O}_2] [\text{PhOH}]^0 \quad (24)$$

The observed results can be explained if the reaction mechanism is extended in a way suggested by Ogata and Morimoto¹⁰ for 2,5-di-tert-butylphenol oxidation by copper complexes:



The deactivation of the complex takes place in the presence of water without a substrate:



The catalyst is regenerated in the presence of phenol:



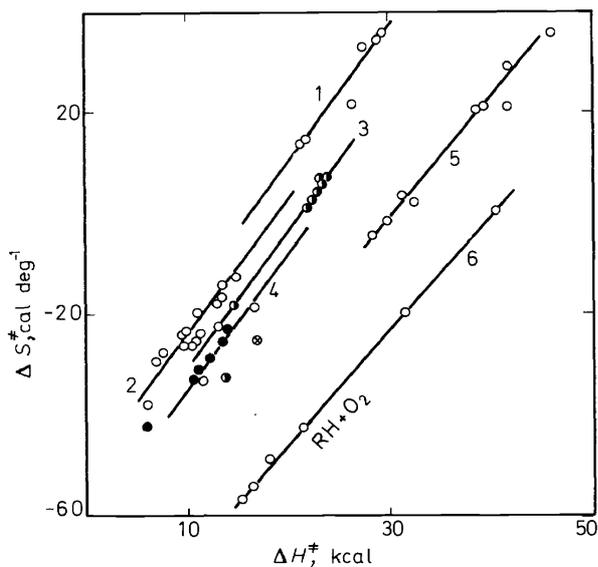


Figure 1. Activation parameters for the oxidation of organic compounds. 1—Co(III), H₂O; 2—Mn(VII), H₂O; 3—V(V), H₂O; 4—Cr(VI), H₂O; 5—Co(acac)₃, non-aqueous medium; 6—RH + O₂, non-aqueous medium.

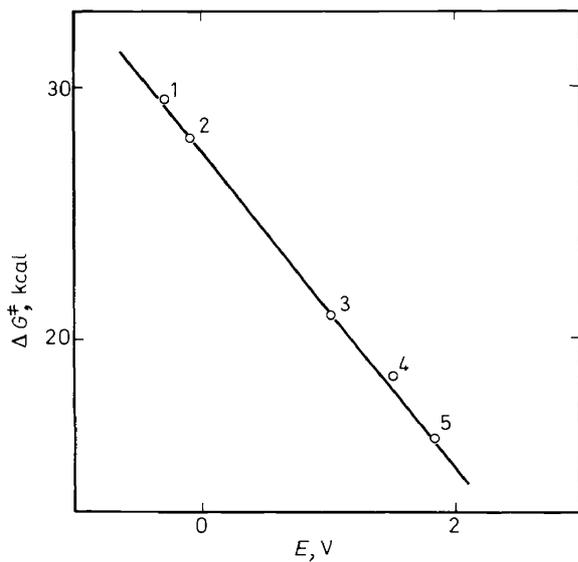


Figure 2. The relationship between activation free enthalpy of the oxidation reaction ($\Delta S^\ddagger = 0$) and the redox potential of oxidizing agent. 1—Co(acac)₃; 2—Co(acac)₂OH; 3—V(V); 4—Mn(VII); 5—Co(III).

COMPARISON OF REACTIVITY OF OXIDATION AGENTS

If the values of activation entropy ΔS^\ddagger found by various authors are plotted against the activation enthalpy values ΔH^\ddagger for different oxidation agents and substrates, then an interesting Leffler's¹¹ correlation is obtained (Figure 1).

If we plot the sections on the ΔH^\ddagger axis (i.e. $\Delta H^\ddagger = \Delta G^\ddagger$; $\Delta S^\ddagger = 0$) against the redox potential of the oxidizing agent a linear dependence is obtained (Figure 2).

It follows that the ligand of the metal complex plays a substantial role in the oxidation process. The molecular oxygen fits well into the series of oxidation agents. It is known¹² that its redox potential (-0.4 V) corresponds to the reaction



which is probably the rate-controlling process.

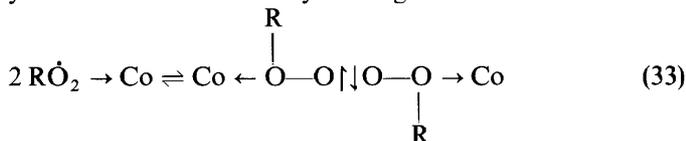
REDUCTION INITIATION

Reaction 4 is widely employed in macromolecular chemistry for the initiation of radical reactions. Till recently it was assumed that the reaction products were free radicals.

This reaction is the main source of radicals during the oxidative degradation as soon as hydroperoxides are formed in the system.

It was first reported by Brandon and Elliot¹³ that $t\text{-BuO}_2^\cdot$ radicals, whose lifetime is as long as several hours, are formed in hydrocarbon solution during the reaction of transition metal acetylacetonates with tert-butylhydroperoxide.

Tkáč *et al.*¹⁴ have shown that the radicals generated in this way decompose through a monomolecular reaction at around 30° to 60°C. At lower temperatures (0°C), however, a diamagnetic dimer is formed which can be transformed reversibly into the active radical by heating:



Complex bonded radicals are stable only in non-polar solvents, i.e. such solvents that are bonded less strongly in the ligand field than the RO_2^\cdot radical.

Recently, we have succeeded in preparing the $t\text{-BuO}^\cdot$ radicals complex-bonded to cobalt via the reaction of di- t -butylperoxalate with $\text{Co}(\text{acac})_2$. The thermal stability of such radicals is even higher than that of complex-bonded $t\text{-BuO}_2^\cdot$ radicals.

REACTIONS OF COMPLEX-BONDED RADICALS

The determining factor of the complex-bonded radical reactivity is the

polarity of solvent. Polarity can be characterized by the donor number¹⁵.

Let us present examples of reactions of complex-bonded *t*-BuO₂[•] radicals:

(a) Replacement reaction

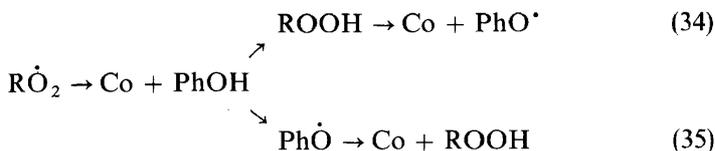
Less reactive polar compounds can replace the RO₂[•] radicals from the ligand field. The relative activity of the polar compound increases in the following order:



The above-mentioned solvents do not react with the RO₂[•] radicals under our reaction conditions (room temperature). These radicals migrate into the solution where they disappear by recombination.

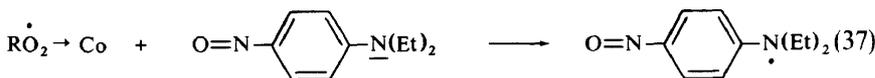
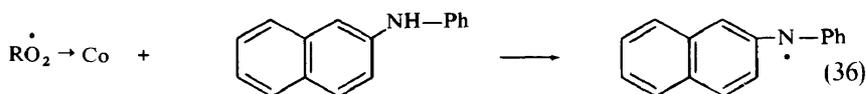
(b) Reaction with phenols

The PhO[•] radical is attached to a cobalt nucleus provided that such attachment is sterically possible¹⁶. It appears as a typical octet in the e.s.r. spectrum. The *o*-substituted phenols, however, produce radicals that participate in further reactions. 2,6-Dimethylphenol¹⁴ produces polyphenyleneoxide radicals. Possible reactions of phenols can be described by the equations:



(c) Reactions with aromatic amines

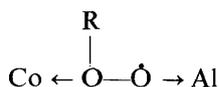
Other reactions studied by us proceed analogously to reaction 34:



(d) Transfer of radicals to other metals

If triethylaluminium is added to the solution of complex bonded *t*-BuO₂[•] radicals, the original singlet seen in the e.s.r. spectrum disappears and a new signal, a sextet, appears ($g = 2.0041 \pm 0.0005$; coupling constant = 2.5 Oe). This signifies that a part of the electron density was transferred to the aluminium nucleus ($I = \frac{3}{2}$).

In this case we assume the formation of a bimetallic complex



The stability of this radical is higher than that of the original $\text{RO}_2^{\cdot} \rightarrow \text{Co}$ radical.

CONCLUSION

It was the purpose of this lecture to describe some reactions of metal compounds in non-polar media. These reactions can also take place in polymer systems. It follows from the facts given that in these systems it is not possible to consider either free metal ions or free radicals.

We believe that only thorough knowledge of the inorganic chemistry of coordination compounds combined with the kinetic experimental data obtained on suitable selected low molecular models can help us to specify all relevant factors that play an important role in polymer systems.

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