COMPLEX-BONDED AND CONTINUOUSLY GENERATED PEROXY AND ALKOXY RADICALS*

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Experimental procedure of selective resolution of "free" and complex-bonded t-$BuO_2^{\bullet}$ and t-$BuO^{\bullet}$ radicals, which are produced during decomposition of peroxides in presence of cobaltous acetylacetonate and di-μ-hydroxotetrakis(acetylacetonato)dicobalt(III) in nonpolar solvents, has been worked out. The radicals coordinated to Co(III) have a prolonged lifetime and their high reactivity can be maintained for several weeks by reducing temperature below 0°C. It is not possible to detect by conventional EPR technique "free" tertiary butylperoxy- and tertiary butoxyradicals, generated continuously by gradual decomposition of peroxides, shortly after mixing the reactants. These radicals of short life time can be indirectly proved after reacting them with phenyl α- or β-naphthylamine (AH) to produce stable radicals. Subsequent and simultaneous reactions in the coordination sphere of associates $[Co(acac)_2]_2$ $[ROOH_2]_n$ and $[Co(acac)_2]_2$ $[AH]_n$ proceed without any diffusion at such a high speed that individual elementary stages of the redox mechanism cannot be at room temperature experimentally followed. Molecular oxygen and polar substances (methanol, water), which solvate outer coordination sphere of transition metals, displace stabilized radicals, whereas blocking the inner sphere during generation of radicals prevents their coordination.

The fundamental problem of the radical decomposition of peroxides at room temperature in nonpolar solvents in presence of transition metals is the assignment of the observed EPR signals to the stationary concentration of "free" radicals continuously generated with short-lifetime[1,2] or the accumulated radical with prolonged lifetime[3], coordinated to the transition metal[4–7]. We made experiments which limit the validity of both theories.

The kinetic conception of Ingold[2] is based on the assumption that in the benzene solution of tertiary butyl hydroperoxide (t-BuOOH) with $Co(acac)_2$ the EPR signals of the t-$BuO_2^{\bullet}$ radicals may be observed only, when the concentration of the non-reacted peroxide is high enough. We proved the existence of the long-lifetime t-$BuO_2^{\bullet}$ and t-$BuO^{\bullet}$ radicals, bound in a Co(III) complex, directly by the EPR method even in absence of peroxides, while "free" radicals of a short lifetime could be proved only indirectly after converting them to more stable radicals of phenyl-β-naphthylamine.

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EXPERIMENTAL AND RESULTS

Purity of reagents as well as preparation of t-$BuO_2^{\bullet}$ from tertiary butyl hydroperoxide, and t-$BuO^{\bullet}$ from di- tert butyl peroxalate was described in previous papers[4-6]. The reaction vessels as well as all the components were prior to reaction freed of oxygen and polar substances, and the processes were carried out under argon atmosphere. An x-band EPR spectrometer Varian E-3 of 100 kc modulation was employed.

Direct Proof of Long-Lifetime t-$BuO_2^{\bullet}$ Radicals in Absence of Tertiary Butyl Hydroperoxide

By mixing 1·7% of toluene solution of $Co(acac)_2$ with 95% solution of tertiary butyl hydroperoxide in molar ratio 1 : 10 at 20°C, a system was prepared, in which concentration of radicals was after 30 minutes $2 \cdot 10^{15}/0 \cdot 3$ ml. The solution was evaporated at room temperature and under vacuum of 10^{-2} Torr to dryness. Green paramagnetic dry residue was dissolved in toluene and the solution was again evaporated in vacuum to dryness. Hydroperoxide may be in this way quantitatively removed from the reaction mixture. On addition of $Co(acac)_2$ to the colourless

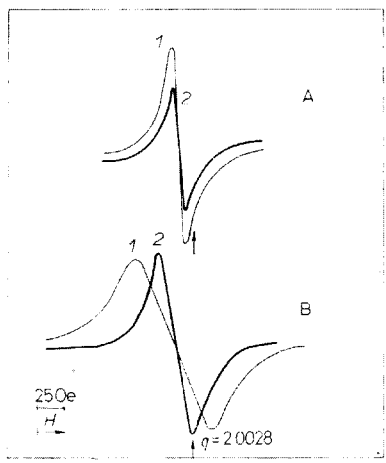


FIG. 1

EPR Signals of Coordinated Radicals $[Co]RO_2^{\bullet}$ in Benzene Solutions without Removal of Hydroperoxide (*1*) and after Removing it by Twofold Vacuum Evaporation (*2*)

(*A*) Original sample: *1* immediately after generation of radicals, *2* on dissolving paramagnetic dry matter in benzene after purification; (*B*) simultaneously prepared samples measured after a 60 min standing at room temperature: *1* unpurified, *2* purified.

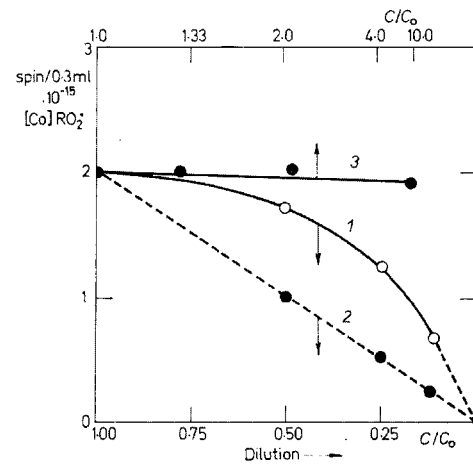


FIG. 2

Dependence of Concentration of Radical Complexes $[Co]RO_2^{\bullet}$ upon Degree of Dilution or Concentration (c/c_0) of Toluene Solutions

1 Dilution by toluene, *2* theoretical curve of dilution for case *1*, *3* vacuum removal of the solvent, c_0 original concentration of radicals immediately after their generation, c concentration after dilution or vacuum concentration of the original sample. Room temperature, concentrations of $Co(acac)_2$ and t-BuOOH 0·04 and 0·40 mol/l, respectively.

first-distillation condensate, the solution turns to green and the t-$BuO_2^{\bullet}$ radicals are generated, while under equal conditions the second-distillation condensate remains colourless and diamagnetic. The dry matter thus repurified has after dissolution in toluene (or CCl_4) the same concentration of radicals as before purification, *i.e.* about 10^{15}/0·3 ml (Fig. 1, A). A simultaneously prepared solution from which hydroperoxide was not removed, exhibited after 60 minutes practically equal t-$BuO_2^{\bullet}$ concentration as the sample without hydroperoxide (Fig. 1, B). The narrowing of the EPR signal is associated with removal of oxygen within the purifying process.

The solution prepared from the purified paramagnetic dry matter at the reduced temperature is diamagnetic, but after a rapid warming from −10°C to 20°C (for about 30 s) original paramagnetism is recovered. The concentration of t-$BuO_2^{\bullet}$ radicals generated immediately during mixing the reactants decreases within 2 hours at room temperature in toluene by about 2 orders of magnitude (10^{13} spin/0·3 ml, in benzene within 3 hours), whereas the purified sample simultaneously kept at 0°C maintains original concentration of radicals even after 2 weeks. Free noncoordinated t-$BuO_2^{\bullet}$ radicals generated by uv radiation from hydroperoxide are irreversibly destroyed at temperatures above −100°C (ref.[8,9]) already. At room temperature no EPR signals are observed 1 min after the radiation had been finished (quartz cell, 300 W- uv lamp, time of irradiation 1—20 min, distance 5 cm). The result is in accordance with studies of other authors[8] (disappearance of signals of t-$BuO_2^{\bullet}$ 1—2 min after switching off the uv lamp).

The purifying process provides no decrease of the high reactivity of the t-$BuO_2^{\bullet}$ radicals to phenols, arylamines, while either stable free phenoxy radicals or complexes of phenoxy radicals with cobalt (octet signal of equal intensity of lines, $I_{Co} = 7/2$) (ref.[10—12]) are produced.

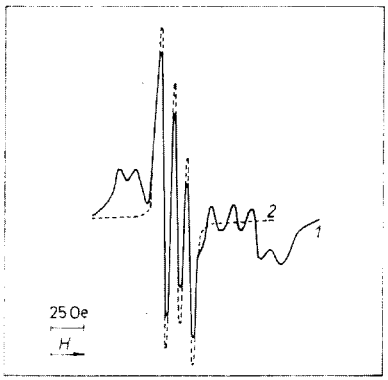


FIG. 3

EPR Signals of Radicals Generated from Phenyl-β-napthylamine (PBN) by Complex-Bonded t-$BuO_2^{\bullet}$ Radicals in Absence (*1*) and Presence (*2*) of Methanol

1 Concentration of PBN 0·54 mol/l, $Co(acac)_2$/PBN 0·1; *2* change of signal after addition of 2 drops of methanol into 0·3 ml of the system.

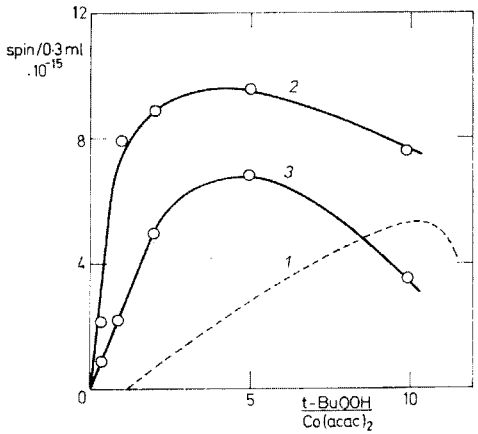


FIG. 4

Plot of Concentration of Paramagnetic Particles against Molar Ratio t-BuOOH/ /$Co(acac)_2$ (EPR Signals: 2 Triplet, 3 Nonet)

1 Generation of [Co]$RO_2^{\bullet}$ radicals in absence of phenyl-β-naphthylamine; *2*, *3* generation of radicals *in statu nascendi* (procedure 3) in presence of PBN (molar ratio PBN/$Co(acac)_2$ 10).

The benzene solution prepared from purified paramagnetic dry matter was gradually diluted or concentrated in vacuum and concentration of the t-$BuO_2^{\bullet}$ radicals (Fig. 2) was examined. Intensity of the EPR signal does not decrease proportionally with the assumed decrease of concentration, but up to the approximately 75% dilution it changes only little; a similar effect may be observed during removal of the solvent. The result is in agreement with the idea on the equilibrium between the complex-bonded radicals and their diamagnetic dimer[4].

Indirect Proof of Continuously Generated Peroxy and Alkoxy Radicals after Reaction with Phenyl-β-naphthylamine

Interaction of t-$BuO_2^{\bullet}$ or t-$BuO^{\bullet}$ radicals with phenyl-β-naphtylamine (PBN) may be accomplished by two procedures[13]: by mixing PBN into the system, where the radicals have been generated (procedure 1), or peroxides are added into the $Co(acac)_2$ solution having a certain amount of PBN already (procedure 2). The experiments are carried out in darkness and under inert atmosphere. For procedure 1, a system is employed, in which undecomposed peroxide was removed by the purifying procedure, whereas if procedure 2 is employed, the radicals are generated *in statu nascendi*. With both procedures, if tertiary butyl hydroperoxide in terms of an oxidating agent is used, a superimposed EPR signal is observed, consisting of a triplet of equal lines intensity ($g = 2{\cdot}0056 \pm 0{\cdot}0003$), and of a nonet having intensity of lines in ratio 1 : 2 : 2 : 2 : 2 : 2 : 2 : 2 : 1 ($g = 1{\cdot}9954 \pm 0{\cdot}0003$). Several drops of methanol remove the nonet from the superimposed spectrum so that the signal formed by three lines of unchanged intensity (Fig. 3) remains. If methanol is added to the reaction mixture containing PBN prior to the excitation of the t-$BuO_2^{\bullet}$ radicals, the three-lines EPR signal only is observed. The nonet signal without a superimposed triplet is observed, when instead of the t-$BuO_2^{\bullet}$ radicals the t-$BuO^{\bullet}$ ones reacted with PBN; consequently, when di-tert-butyl peroxalate is employed in terms of an oxidating agent.

Dependence of concentration of the t-$BuO_2^{\bullet}$ radicals upon molar ratio of reactants generated in absence or presence of PBN($Co(acac)_2$/PBN 10, procedure 2) is compared in Fig. 4. Whereas in absence of PBN the measurable level of t-$BuO_2^{\bullet}$ radicals is observed only for t-BuOOH/ /$Co(acac)_2$ > 1 and maximum of the concentration (of about $5 \cdot 10^{15}/0{\cdot}3$ ml) is at room temperature for the molar ratio 10, the concentration of radicals in the maximum shifted towards molar ratio 5 is higher ($10^{16}/0{\cdot}3$ ml) in presence of PBN. Under these conditions the radicals are generated also in excess of $Co(acac)_2$ (t-BuOOH/$Co(acac)_2$ < 1). With the increasing concentration of PBN also concentration maximum of the radicals increases up to a certain limit value.

DISCUSSION

EPR Signals and Theory of Continuously Generated Radicals

The experimental fact that the EPR signals of highly active t-$BuO_2^{\bullet}$ radicals may be observed within several hours in nonpolar solutions at room temperature also in systems freed of the undecomposed tertiary butyl hydroperoxide, cannot be explained by kinetic theory suggested by Ingold[2] for the system considered. A series of experiments speak against this explanation based on higher stationary concentration of $[t\text{-}BuO_2^{\bullet}]_s$ radicals in presence of Co(II), provided that the steadily decomposing hydroperoxide is a source of peroxy radicals:

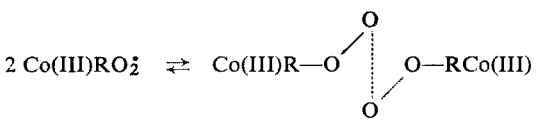
1. The amount of excited peroxy and butoxy radicals is not proportional to the concentration of hydroperoxide[4] and peroxalate[6], respectively, but dependence of intensity of the EPR signal upon molar ratio of the reactants passes the maximum.

2. In the photometric and conductometric titrations of hydroperoxide with $Co(acac)_2$, concentration of hydroperoxide decreases and the stationary concentration of $[t\text{-}BuO_2^{\bullet}]_s$ should thus decrease, too. Unlike this, the level of radicals at the beginning rises during titration; accumulation of them takes place even if there are great time intervals (within which „free" radicals could be destroyed by recombination) between individual measurements during the titration.

3. The level of radicals is neither proportional to the concentration of Co(II). After a ten-fold decrease of the $Co(acac)_2$ concentration, the same level of radicals[4] is generated. Even at the highest concentration of radicals generated cobalt is in the system present in the oxidized form Co(III) (ref.[7]). Functional dependence for the stationary concentration of radicals does not fit to kinetic theory $[RO_2^{\bullet}]_s = f\{[Co(II)] \,.\, [t\text{-}BuOOH]\}$.

4. Because of the activation energy of initiation being greater than that of the termination, $E_i < E_t$, the increase of temperature should lead according to the kinetic theory to a higher stationary concentration of radicals. This effect, however, is not observed. Above 30°C, the EPR signals irreversibly disappear, with the effective activation energy of 28 kcal/mol.

5. Disappearance of paramagnetism, if temperature is reduced below 0°C, and its immediate many times repeated recovery to the original value (30 s) cannot be explained by a decrease of the rate of initiation R_i. Maximum value of radicals can be at room temperature attained within 10 to 30 min according to the efficiency in maxing; the process is at the outset accompanied by formation of oxygen, this leading to the broadening of the EPR signals ($2\ t\text{-}BuO_2^{\bullet} \rightarrow 2\ t\text{-}BuOOBu\text{-}t + O_2$). This effect is not observable for reversible recovery of the signal. The reversible change of paramagnetism with temperature without any oxygen evolution is well explained by equilibrium reaction of dimerization, the tetroxide being produced[4]. As confirmed



(*A*)

by stable concentration of radicals during dilution and condensation, this equilibrium exists even at room temperature. Decrease of temperature results in shifting equilibrium towards the diamagnetic dimer.

6. In the reaction of di-μ-hydrotetrakis(acetylacetonato)dicobalt(III) with hydroperoxide, the $t\text{-}BuO_2^{\bullet}$ radicals of short lifetime are produced (1 to 2 minutes on mixing the reactants, the original EPR signal decreases down to a very low value) and a vigorous evolution of oxygen simultaneously takes place (coordination of radicals in the system is not possible).

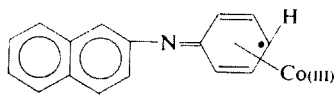
7. Di-tert-butyl peroxalate is thermally decomposed under formation of $t\text{-}BuO^{\bullet}$ radicals. The rate of termination of these radicals[14–16] is considerably higher than that of the $t\text{-}BuO_2^{\bullet}$ radicals, $[R_t^{BuO^{\bullet}}] = 10^{-9}\ l\ mol^{-1}\ s^{-1}$; however, concentration of generated butoxy radicals in presence of $Co(acac)_2$ is at room temperature high and the signal may be observed relatively for a long time even at elevated temperature (up to 90°C). Decrease of temperature below −40°C does not lead to disappearance of paramagnetism, because in this case no diamagnetic tetroxides can be produced.

8. In presence of polar substances in the reaction mixture, generation of long-lifetime radicals cannot be made.

Coordinated and Continuously Generated Radicals Indicated by Indirect Method

The indirect method of detecting the radicals in presence of phenyl-β-naphthylamine showed (procedure 2) that total level of radicals thus indicated is about 4 times higher than that achieved in the interaction of complex-bonded t-$BuO_2^{\bullet}$ radicals with PBN (procedure 1). This fact is confirmed by presence of realy "free" radicals in the reaction system and by justification of the theory of continuous generation, provided that nonstabilized radicals of a short lifetime cannot be detected by conventional EPR technique. The signals examined for a long time (for example after 10 min) must be solely ascribed to radicals coordinated to cobalt. In presence of polar substances (methanol) which are preferably coordinated to cobalt, the oxidation of $Co(acac)_2$ with hydroperoxide does not lead to the formation of EPR signals, even though a parallel experiment in presence of PBN confirms that a relatively high concentration of free short-living radicals was produced by the redox step.

Analysis of the superimposed EPR signal has been studied in another paper[13] of ours and we came to a conclusion that ratio of planes of both signals, triplet/nonet, which alters with reaction conditions, expresses ratio $RO_2^{\bullet}/RO^{\bullet}$ of the radicals present in the system. The signal formed by three lines belongs to stable nitroxy radicals of the $Ar_1—\overset{\overset{\displaystyle O^{\bullet}}{|}}{N}—Ar_2$ type, whereas the nine-lines signal belongs probably to the radical complex of the resonance form of amino-radicals with cobalt (a_{Co} = 14 Oe, a_H = = 13 Oe, octet split into a doublet) of type



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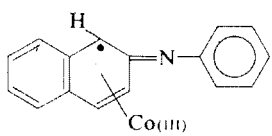


because interaction of the unpaired electron with nitrogen nucleus is on the basis of EPR spectra negligible. The complex decomposes in presence of methanol and the amino-radicals thus released are destroyed by recombination or they react with the present $RO_2^{\bullet}$ radicals [17,18]

$$RO_2^{\bullet} + {}^{\bullet}N \rightarrow RO^{\bullet} + NO^{\bullet}. \qquad (D)$$

In the generation of radicals *in statu nascendi* (procedure 2) a double amount of the nonet signal than of the triplet signal is produced; consequently the RO• radicals as primary products of the break of peroxidic bond react preferably with PBN than with hydroperoxide. This reaction is preferred to the electron transfer RO• + Co(II) → RO$^{(-)}$ Co(III), this fact accounting for the possibility to generate radicals even if $Co(acac)_2$ is in excess with respect to hydroperoxide.

The indirect proof of the radical mechanism of the peroxides decomposition could be used also for oxidation of $Co(acac)_2$ with benzoyl peroxide. In this reaction, concentration of free radicals (which have no possibility to be coordinated) is of such a low level that in absence of PBN, the EPR signals cannot be observed; unlike this, presence of PBN provides generation of an intense triplet of NO• radicals.

EPR Signals of Coordinated Radicals

Let us analyze the problem of complex-bonded radicals from the viewpoint of EPR spectral parameters. Let us assume that coordination to cobalt is accomplished by a pair of nonbonding electrons both for t-BuOO• and t-BuO• radicals. Since in case of a tertiary butyl peroxy radical the spin density of unpaired electron is more concentrated to external oxygen[18], coordination through internal oxygen does not virtually change value of the g-factor, when compared with that of „free" light-generated radicals. Unlike this, in the coordination of butoxy radicals through oxygen with the unpaired electron, a g-factor higher by $0{\cdot}0018 \pm 0{\cdot}002$ is observed. Little changes of g were studied by Hoffman and Eames[19] during stabilization of nitroxy radicals on $AlCl_3$.

Direct interaction of the unpaired electron with a magnetic moment of the nucleus may be accomplished only through s-orbits or sp-hybridization. This condition is not fulfilled in the coordination to a free cobalt d-orbit. The hyperfine structure was not observed either during generation of a complex of a free radical of di-tert-butylnitroxide with Co(II) (in terms of a coordinated ligand[20]). By transferring the $BuO_2^{\bullet}$ radicals from Co to Al, however, we obtained a six-lines EPR spectrum[5] characteristic for interaction with the aluminium nucleus ($I = 5/2$). Interaction of the unpaired electron with the cobalt nucleus ($I = 7/2$), as has been shown by us in ref.[6,10,12], may be proved for complexes of cobalt with phenoxy radicals which have no bulky substituent in the *para*-position (octet EPR signals), as well as for complexes of aromatic amino radicals generated from PBN (ref.[13]). Individual lines of the octet are further split from protons of the benzene nucleus. A quantum-chemical analysis of the problem only can determine, whether the magnetic moment of the cobalt nucleus interacts with the unpaired electron *via* its 4s-orbital through π-system of the benzene ring, or directly through oxygen of appropriate phenoxy radical. In polar solutions (H_2O, methanol), the phenoxy radicals of nitrophenols produce complexes of radicals with pentacyanocobaltate(II) (ref.[21–23], the interaction both with the

cobalt nucleus and with the nitrogen nucleus and protons on the benzene ring being at the same time observed). In polar solvents Czapski[24], using a rapid flow method, proved existence of complex radicals of type Me-$HO_2^{\bullet}$ on Nb(V) and La(III), having a well differentiated hyperfine structure which characterizes interaction with the relevant nuclei (10- and 8-lines spectra). In these experiments, intensity of the EPR signals increases at the outset with concentration of hydrogen peroxide and afterwards, it decreases down to zero. This course through a maximum is in accordance also with our study within preparation of radical complexes on cobalt, the difference, however, consists in the fact that in nonpolar solvents, the complexes have a much longer lifetime, whereas in polar solvents, the EPR signals can be detected only with use of a conventional or rapid "flow" method[25–30]. Coordination of oxygenous $HO_2^{\bullet}$ radicals on Ti(IV) was proved by Fischer[31]; recently, the possibility to stabilize radicals of a lifetime of several weeks at room temperature in presence of metals Cu(II), Fe(III), and La(III) has been pointed out by Bartelink and coworkers[32]. It has been shown that with these complexes, metal does not affect the hyperfine structure of the spectrum and the unpaired electron is assumed to be localized on the π-orbit. Whether the unpaired electron of oxygenous radicals interacts with magnetic moment of the metal nucleus, obviously depends on steric properties of coordinated radicals. An interaction of $O_2^{(-)\bullet}$ and $HO_2^{\bullet}$ but not of t-$BuO_2^{\bullet}$ and t-$BuO^{\bullet}$ on cobalt may be, for example, observed. Exact theoretical interpretation of these complexes remain an open quantum-chemical problem.

Radical Reactions in Complexes

Radical reactions in the coordination sphere of transition metal complexes proceed with a low activation energy. When studying these reactions we failed to prove by conventional EPR technique the primary product of homolytic splitting of the peroxidic bond during reduction of the latter, *i.e.* the $RO^{\bullet}$ radicals, neither if the reaction was carried out at reduced temperature directly in the resonance cavity. The EPR signals of the $RO_2^{\bullet}$ radicals, only, may be obesrved from the first moment after mixing the reactants.

If we consider that dimer $[Co(acac)_2]_2$ forms complexes with hydroperoxides, PBN (ref.[13]), oxygen[33] as well as with alcohol (composition of these associates depends on molar ratio of the reactants similarly as concentration of generated radicals), we are able to explain formation of products of the redox mechanism by redistribution of electrons in complexes. This conception of multistage reactions in the coordination sphere is supported by findings of Okubu and coworkers[34] who, using the MO EH method, examined question of nucleophilic or electrophilic attack of dimer $[ROOH]_2$ to which a lower stability than to monomer is assigned. The dimer forms a 6-membered ring through two hydrogen bridges. Even though Co(II) has an unpaired $3d^7$ electron, its dimer does not provide an EPR signal and its high stabi-

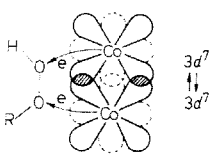
lity is therefore assumed to be connected with interaction of both unpaired spins, provided that a partial overlapping of both $3d^7$ orbits takes place. Hydroperoxide can be coordinated by a pair of a nonbonding electron into free antibonding orbits, provided that requirements of symmetry are fulfilled[35,36].

On the basis of the assumptions made, it is possible to suggest Schemes 1–4 for four types of reactions in the coordination sphere, proceeding stoichiometrically under formation of free radicals which remain either complex-bonded or free, according to whether unoccupied coordination places are available or not.

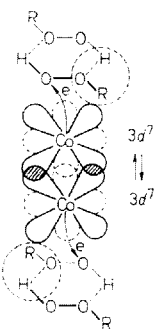
In dilute solutions (particularly at elevated temperature and in polar solvents) equilibrium of reaction $2\ ROOH \rightleftarrows [ROOH]_2$ is shifted towards formation of the monomer. If $Co(acac)_2$ is simultaneously in excess with respect to hydroperoxide, the $RO^{\bullet}$ radicals, generated in the primary coordination step, are deactivated immediately in the coordination sphere by transfer of electron from the second Co(II) atom in the dimer. For t-BuOOH/$Co(acac)_2 < 1$, the redox reaction proceeds without detection of EPR signals and after the reaction, electric conductivity of the system considerably rises[7]:

$$[CoL_2]_2 + ROOH \rightarrow L_2CoOH + L_2CoOR\,. \qquad (E)$$

Hydroperoxide is coordinated mostly as dimer, if used concentrated, and t-BuOOH/$Co(acac)_2$ is $\gg 1$. In addition to the redox step, also induced decomposition of hydroperoxide takes place at room temperature and in a ten-fold excess of hydroperoxide, the $RO_2^{\bullet}$ radicals being formed. Maximum of radicals may be seen after association of four dimers, which is in accordance also with determination of the point of equivalence in the photometric titration[7]. Dimer is decomposed under formation of coordinated radicals into hydroxiderivatives of Co(III) and tertiary butyl alcohol. Alcohol gradually displaces the $RO_2^{\bullet}$ radicals from the coordination sphere.



SCHEME 1



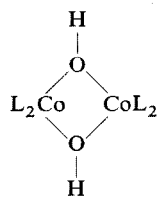
SCHEME 2

The recombining $RO_2^{\bullet}$ radicals may lead to the formation of oxygen which also can block coordination places.

$$[CoL_2]_2\ 2[ROOH]_2 \rightarrow 2[RO_2^{\bullet}]L_2CoOH + 2\ ROH\,. \qquad (F)$$

In presence of antioxidants of the AH type, the primarily produced $RO^{\bullet}$ radicals generate radicals $A^{\bullet}$, even when $Co(acac)_2$ is in excess with respect to hydroperoxide. In the coordination sphere the electron transfer from Co(II) to radical (Scheme 1) as well as induced decomposition (Scheme 2) are suppressed.

$$[CoL_2]_2[AH]_2 + 2\ ROOH \rightarrow$$

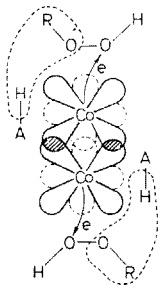


$$+ 2\ ROH + A^{\bullet}\,. \qquad (G)$$

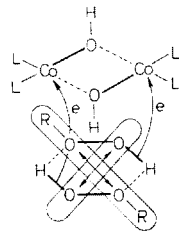
At elevated temperature the catalytic cycle is closed through di-μ-hydroxotetrakis-(acetylacetonato)dicobaltate(III) (ref.[7]) "Free" $RO_2^{\bullet}$ radicals are produced, which recombine under evolution of molecular oxygen.

$$[CoL_2OH]_2\ [ROOH]_2 \rightarrow [Co(acac)_2]_2\ 2[H_2O] + ROOR + O_2\,. \qquad (H)$$

The transfer of a *d*-electron from a transition metal onto *p*-orbit a of free radical proceeds in considered complexes with a relatively low activation energy, the subsequent and simultaneous reactions being accomplished in the coordination sphere without classic diffusion of the reactants. For that reason, it is possible, immediately during the mixing process, to achieve at room temperature and under optimum conidtions a relatively high concentration of complex-bonded radicals (about 2.



SCHEMA 3



SCHEME 4

. 10^{-4} mol/l), even when the concentration remains nearly by two orders of magnitude lower than it would correspond to the quantity of Co(II) present in the system (4 . 10^{-3} to 10^{-2} mol/l). We therefore assume that approximately as high as 99% of primary-generated radical complexes are decomposed already within generation of them, which is most probably associated with exothermic character of oxidation of cobalt(II) and thus with local overheating of the system within mixing the components (radical complexes above 30°C are decomposed irreversibly). Later on, the coordinated radicals are displaced by polar products. On releasing the radical from a complex, the catalyst, which gradually decomposes excess of hydroperoxide without fixation of radicals (Scheme 4), is accumulated in the system. Concentration of 8 . 10^{-4} mol/l of accumulated stable radicals A$^{\bullet}$ indicated by indirect EPR method is therefore a sum of a complex-bonded radicals, "free" radicals as products of decomposition of complexes, as well as radicals continuously generated by catalytic decomposition of hydroperoxide. When summing up what has been said, however, it is necessary to take into account also preference of the hydrogen transfer from AH to RO$^{\bullet}$ to the removal of radicals by the electron transfer (Scheme 1 and 3).

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