

DECOMPOSITION MECHANISM OF PEROXIDES IN PRESENCE OF Co(II) ACETYLACETONATE*

R. PŘIKRYL^a, A. TKÁČ^a, L. MALÍK^a, L. OMELKA^a and K. VESELY^b

^a *Institute of Chemical Physics,*

Slovak Technical University, 880 32 Bratislava and

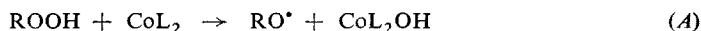
^b *Research Institute of Macromolecular Chemistry, 600 00 Brno*

Received June 4th, 1973

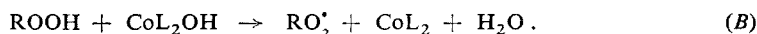
Decomposition of tertiary butyl hydroperoxide in presence of cobaltous acetylacetonate proceeds at room temperature in nonpolar solvent as stoichiometric reaction, whereas at higher temperatures in terms of a catalytic reaction, *via* redox cycle $\text{Co(II)} \rightarrow \text{Co(III)} \rightarrow \text{Co(II)}$. Primary product of oxidation is here di- μ -hydroxotetrakis(acetylacetonato)dicobalt(III). At the temperature of the ambient, nearly all the cobalt is in excess of hydroperoxide present in the oxidized form. These conditions are most convenient for accumulation of tertiary butylperoxy radicals BuO_2^* which are produced in the elementary stage of reduction of peroxidic bond, provided that in the coordination sphere of Co(III) free coordination places are present. From this viewpoint also decomposition mechanism of di-tertiary butyl peroxalate and benzoyl peroxide has been studied.

In spite of the fact that many authors^{1,2} were concerned with the question of redox reactions between hydroperoxides and transition metal compounds, the present state of knowledge on these reactions remains greatly incomplete.

Cobalt is a typical representative of transition metals, which can react with hydroperoxides either as reducing agent



or in terms of the oxidizing agent



Further reactions of radicals RO^* and RO_2^* result in the formation of a variety of products, the most important of which are: tertiary butyl alcohol (produced by reaction of RO^* with some of hydrogen donors present in the system) and oxygen (produced by recombination of RO_2^* radicals). Considerably less studied is effect of the coordination sphere of cobalt on the course of these reactions.

In polar acetic acid medium, cobalt is in case of cobaltous acetate³⁻⁵ and cobaltous acetylacetonate⁶ present mostly as Co(II) in the final mixture. Only if in terms of a reducing agent

* Part IV in the series Radical Reactions in the Ligand Field of Transition Metals; Part III: 39, 3504 (1974).

$K_2Co(II)$ ethylene diamine tetraacetate was employed, cobalt in the final mixture was present as $Co(III)$. Various authors found great differences in the state of oxidation of cobalt in final reaction mixture of nonpolar solutions. Richardson⁷ employed 2-ethylhexanoatocobaltate(II) in chlorobenzene and in the equilibrium mixture he found 52 to 55% of $Co(III)$ polarographically as well as by measuring ratio of optical densities D_{375}/D_{608} . For $Co(acac)_2$ in benzene, Osawa⁶ assumes cobalt to be present in the final mixture also as trivalent. By using reaction of $Co(II)$ with ammonium thiocyanate, Bulgakova and coworkers⁸ found that at enhanced temperature only 12–15% $Co(III)$ is involved in the final mixture during reaction of decyl hydroperoxide with $Co(acac)_2$ in *n*-decane. This analytical method for determination of $Co(II)$ was before used by Ščeredin and Denisov⁹.

Only in nonpolar medium, coordinated radicals^{10,11} $[BuO_2^*]Co(III)$ which were destroyed after addition of polar substances, were examined more extensively. In the reaction of $Co(acac)_2$ with peroxalate¹², long-life radicals BuO^* are produced, which are likewise destroyed on addition of polar substances into the system.

EXPERIMENTAL

Reagents

Preparation of cobaltous acetylacetonate, tertiary butyl hydroperoxide, and di-tert-butyl peroxalate has been described in previous papers^{11,12}. Deuterated solvents C_6D_6 and $CDCl_3$

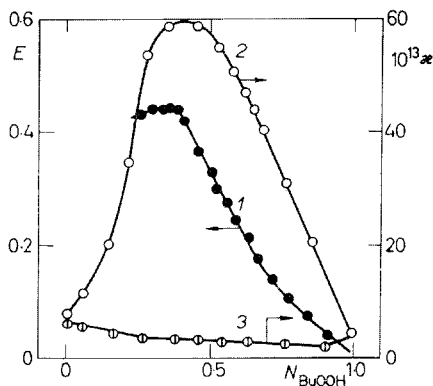


FIG. 1

Plot of Extinction E_{596} and D. C. Conductivity ($\Omega^{-1} \text{ cm}^{-1}$) against Mole Fraction N_{BuOOH}

1, 2 Binary mixture with $Co(acac)_2$, 3 with $Co(acac)_3$; titration of *t*-BuOOH solution (10^{-3} mol/l) with $Co(acac)_2$ solution (10^{-2} mol/l), 20°C , concentration of solutions during measurement of conductivity, 10^{-2} mol/l .

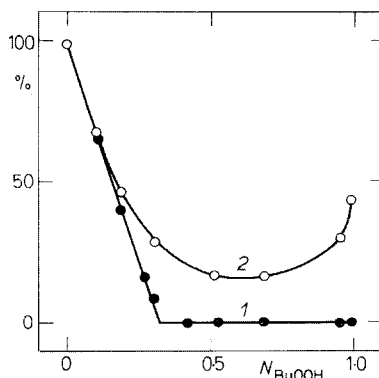


FIG. 2

Plot of Ratio of Nonreacted Cobaltous Acetylacetonate against Mole Fraction N_{BuOOH}

Concentration of $Co(acac)_2$ established photometrically (596 nm): 1 indirectly by determining concentration of $Co(acac)_3$, 2 by reaction with ammonium thiocyanate.

(Isocomerz Berlin), benzoyl peroxide and tertiary butyl peroxide (Lachema, Brno and Schuchardt München); di- μ -hydroxotetrakis(acetylacetonato)dicobalt(III) was prepared according to Boucher and Herrington¹³ by oxidation of $\text{Co}(\text{acac})_2$ with hydrogen peroxide at 25°C in methanol in presence of potassium acetate.

Photometric and Conductometric Titrations of Peroxides with Cobaltous Acetylacetonate

Trivalent cobalt was quantitatively determined with spectrophotometer Specol (C. Zeiss Jena, spectral half-width 11 nm, temperature of the ambient), making use of absorption band 596 nm. Conductometric titration was carried out in nitrogen atmosphere in a combined measuring cell¹⁴ tempered to 20°C. Specific conductivity was calculated from a resistance value (teraohmometer BM-283 Tesla, Brno) determined 1 min after applying d.c. voltage. The conductivity was determined with a limit error $\pm 10\%$, and precision of results was $\pm 3\%$.

Infrared, NMR, and EPR Spectra

Infrared spectra (UR-10 C. Zeiss, Jena) were measured in KBr cells (0.624 and 0.602 mm thick). The NMR spectra (Tesla BS-487, 80 Mc) were determined in deuterated solvents using modulation of magnetic field by a superstabilizer with calibration of resonance bands involving the side-band method, or by modulation of frequency employing proton stabilization. As internal standard hexamethyl disilane was employed for the determination of chemical shift. The EPR signals were measured on x-band spectrometer Varian E-3 of 100 kc modulation.

RESULTS

Reactions of Tert-butyl Hydroperoxide with Cobaltous Acetylacetonate at Room Temperature

When titrating benzene solutions of tert-butyl hydroperoxide and cobaltous acetylacetonate(II) using spectrophotometric indication, the point of inflexion was observed for molar ratio $\text{Co}(\text{II})/\text{-BuOOH}$ equal to $2(N_{\text{BuOOH}} = 0.33, \text{Fig. 1})$, irrespective of the fact whether hydroperoxide was added into excess of acetylacetonate or *vice versa*.

The amount of nonreacted $\text{Co}(\text{II})$ was also established by analysis always as late as three hours after mixing the reactants. Curve 1 (Fig. 2), which indicates percentage of nonreacted $\text{Co}(\text{II})$ against composition of the reaction mixture, was constructed on the basis of the differences between original acetylacetonate concentration, $(\text{Co}(\text{II}))_0$, and that of $\text{Co}(\text{III})$ found photometrically. Curve 2 denotes % of nonreacted $\text{Co}(\text{II})$ determined directly from the thiocyanate complex⁸. Comparison of the curves points to a disagreement in systems with excess of hydroperoxide. The reaction with thiocyanate is therefore not selective for quantitative determination of $\text{Co}(\text{II})$. Because of $\text{Co}(\text{acac})_2\text{OH}$ being the primary product of reaction (A), we paid our attention to checking the influence of this substance upon reaction with thiocyanate. By stepwise addition of a colourless NH_4SCN solution into a green $\text{Co}(\text{acac})_2\text{OH}$ solution, extinction at 596 nm up to molar ratio 1 : 1 increases (Fig. 3, curve 1),

whereas by addition of $\text{Co}(\text{acac})_2$, the complex at molar ratio 1 : 2 (Fig. 3, curve 2) is produced. The molar extinction coefficient of complex $[\text{Co}(\text{acac})_2\text{OH}]_2$ with ammonium thiocyanate amounts to $5.2 \cdot 10^2 \text{ l mol}^{-1}\text{cm}^{-1}$, which is a value about half of that of complex $\text{Co}(\text{acac})_2 \cdot 2 \text{ NH}_4\text{SCN}$ for which values $1.15 \cdot 10^3 \text{ l mol}^{-1}\text{cm}^{-1}$ (ref.⁸) and $1.25 \cdot 10^3 \text{ l mol}^{-1}\text{cm}^{-1}$ (ref.⁹) were published. Completely coordinated $\text{Co}(\text{acac})_3$ does not react with thiocyanate.

The NMR spectra of mixtures of 0.2 mol/l solutions of *t*-BuOOH in deuterated benzene with $\text{Co}(\text{acac})_2$ of equal concentration confirm that for the $\text{Co}(\text{II})/\text{t-BuOOH}$ ratio 2, the stationary concentration of $\text{Co}(\text{III})$ is settled, which no more changes on adding further *t*-BuOOH (Fig. 4). The only broad line of chemical shift $\delta \approx 0$ p.p.m., belonging to the CH_3 protons in the ligand, changes after the reaction with *t*-BuOOH into many narrow lines of $\delta = 1.6 - 2.2$ p.p.m. In the redox step $\text{Co}(\text{II}) \rightarrow \text{Co}(\text{III})$ original paramagnetism of $\text{Co}(\text{acac})_2$ disappears and the half-width of individual lines consequently decreases. If hydroperoxide is in excess, $[\text{t-BuOOH}]/\text{Co}(\text{II}) = 2$,

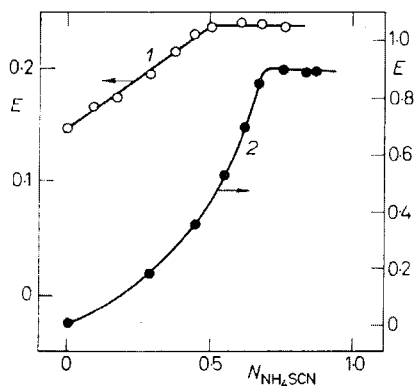


FIG. 3
Plot of Extinction E_{596} against Mole Fraction of Ammonium Thiocyanate in a Binary Mixture with $\text{Co}(\text{acac})_2\text{OH}$ (1) and with $\text{Co}(\text{acac})_2$ (2).

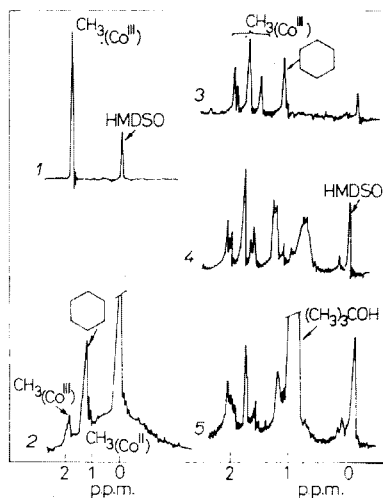


FIG. 4
NMR Spectra of Reactants and Their Mixture

Solutions in deuterated benzene (0.2 mol/l), 20°C: 1 $\text{Co}(\text{acac})_3$; 2 $\text{Co}(\text{acac})_2$; 3 reaction mixture $\text{Co}(\text{acac})_2$ with BuOOH (molar ratio 2); 4 reaction mixture for molar ratio 1; 5 reaction mixture for molar ratio 0.2.

broadening of lines, due to release of oxygen, is again observed (the effect may be avoided by bubbling nitrogen through the solution).

Two lines of different chemical shift (region 5 to 5.3 p.p.m.) correspond to protons of the $=\text{CH}$ group of acetylacetonate ligand, which gives evidence of the formation of more Co(III) derivatives. A further band, whose intensity, half-width, and chemical shift changes with the concentration change of the reaction products, as well as with time (0.3–1.0 p.p.m.) can be removed by distilling off liquid components in vacuum which predominantly produce tertiary butyl alcohol beside nonreacted $t\text{-BuOOH}$, if the latter was in excess. Changes in value of the chemical shift of CH_3 groups of t -butyl alcohol are due to intramolecular association (Fig. 5) and to the linkage of butanol to the coordination sphere of Co(III). Dry residue was after removal of the liquid phase further separated by fractional crystallization ($\text{CCl}_4 + \text{C}_6\text{D}_6$) and relevant NMR spectra confirm the multicomponent nature of the Co(III) products. In Fig. 6, the NMR spectra of fractional oxidation products are compared with the

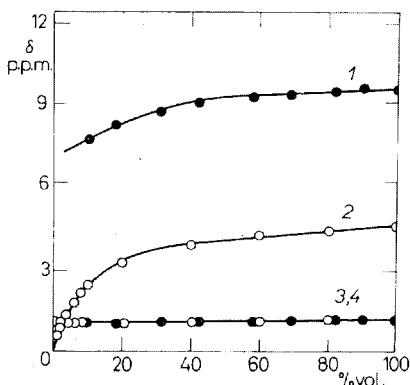


FIG. 5

Plot of Chemical Shift δ against Concentration of Solvent C_6D_6 During Dilution of tert-Butyl Peroxide and tert-Butyl Alcohol $t\text{-BuOOH}$: 1 —OH; 2 — CH_3 ; $t\text{-BuOH}$: 3 —OH; 4 — CH_3 .

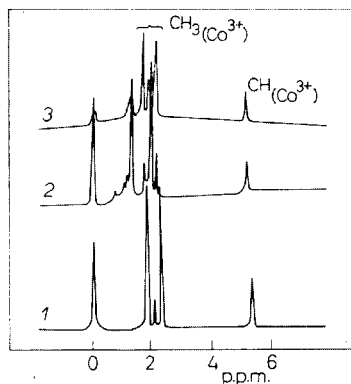


FIG. 6

NMR Spectra of Di- μ -hydroxotetrakis(acetylacetonato)dibalt (III) and Reaction Mixture Components after Fractional Crystallization

1 $[\text{Co}(\text{acac})_2\text{OH}]_2$, 0.1 mol/l in CDCl_3 ; 2 products of reaction of $\text{Co}(\text{acac})_2$ with hydroperoxide on removing liquid portions in the phase richer for CCl_4 during fractional crystallization in the ($\text{C}_6\text{D}_6 + \text{CCl}_4$) mixture in equimolar ratio; 3 see for 2 in the part richer for C_6D_6 .

$[\text{Co}(\text{acac})_2\text{OH}]_2$ spectrum which is in accordance with that described by Boucher and Herrington¹³.

Appearance of narrow lines associated simultaneously with disappearance of original broad band at 0 p.p.m. (in excess of *t*-BuOOH) is a further indirect proof that in the system, no paramagnetic Co(II) in a significant concentration is present. If both components are mixed in an opposite sequence [$\text{Co}(\text{acac})_2$ is added to *t*-BuOOH in excess], somewhat differing NMR spectra of the oxidation products of cobalt are observed. The ratio of band intensities of $=\text{CH}$ and the CH_3 acetylacetonate ligand is changed.

The starting components may be distinguished from the reaction products by using infrared spectra (Fig. 7). The most distinct difference¹⁵ between $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{acac})_3$ is observed in spectral region of 400 to 700 cm^{-1} . Symmetric $[\text{Co}(\text{acac})_2$.

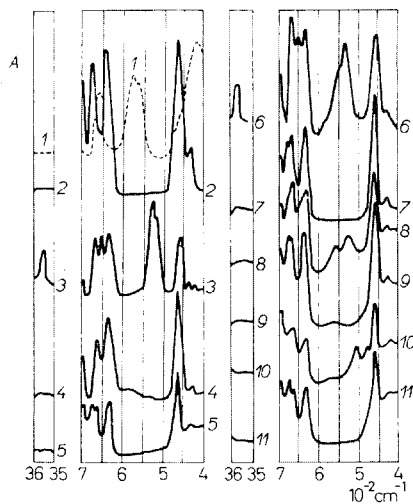
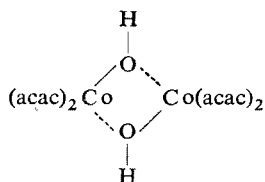


FIG. 7

Infrared Spectra of Starting Components (1—3) and Reaction Products (4—11) in the Oxidation of $\text{Co}(\text{acac})_2$ by Peroxides or Oxygen in Tetrachloromethane

1 $\text{Co}(\text{acac})_2$; 2 $\text{Co}(\text{acac})_3$; 3 $[\text{Co}(\text{acac})_2\text{OH}]_2$; 4 $[\text{Co}(\text{acac})_2\text{OH}]_2$ on heating up; 5 oxidation of $\text{Co}(\text{acac})_2$ at 20°C and irradiation with uv light; 6 spectrum of a reaction mixture of *t*-BuOOH with $\text{Co}(\text{acac})_2$ (1 : 2) after distilling off tert-butyl alcohol; 7 sample as for 6 after thermal decomposition; 8 reaction mixture of di-tert-butyl peroxalate with $\text{Co}(\text{acac})_2$ (1 : 2) on removing tertiary butyl alcohol; 9 sample as for 8 after thermal decomposition; 10 reaction mixture of benzoyl peroxide with $\text{Co}(\text{acac})_2$ (1 : 4) on drying in vacuum and redissolving dry material; 11 sample as for 10 after thermal decomposition. Thermal decomposition at the boiling point of tetrachloromethane (77°C) and after evaporation, the evaporated matter was maintained at 100°C for 20 minutes.

$\cdot\text{OH}]_2$ is in the solution of tetrachloromethane characterized by an intense band of 530 cm^{-1} which is ascribed to skeleton vibration¹³ of the dimer cycle



Valency OH vibrations are observed at $3\,570\text{ cm}^{-1}$. In the reaction of t-BuOOH with $\text{Co}(\text{acac})_2$ being in molar ratio 1 : 2, the infrared spectrum with typical dimer cycle bands $[\text{Co}(\text{acac})_2\text{OH}]_2$ is achieved after removal of volatile products (Fig. 7, curve 6).

It follows from the titration and spectral measurements (NMR and IR spectra) presented that in a nonpolar solvent the reaction with cobaltous acetylacetonate has at room temperature a stoichiometric character.

In excess of $\text{Co}(\text{acac})_2$, a fast reaction⁹ between free radicals and cobalt $\text{RO}_2^{\cdot} + \text{Co}(\text{II}) \rightarrow \text{RO}_2^- + \text{Co}(\text{III})$ takes place and consequently, formation of long-living BuO_2^{\cdot} radicals may be observed by EPR method¹¹ at low $\text{Co}(\text{II})$ concentration only. The amount of radicals depends on absolute concentration of reactants and at high concentrations even upon method of their mixing. During addition of $\text{Co}(\text{acac})_2$ into t-BuOOH (Fig. 8, curve 1), maximum of the BuO_2^{\cdot} concentration appears at molar ratio t-BuOOH/ $\text{Co}(\text{II})$ being equal to 4. By further addition of $\text{Co}(\text{II})$ the maximum gradually decreases down to zero ($N_{\text{BuOOH}} = 0.5$). Position of maximum is shifted with concentration of hydroperoxide, which itself is a strongly polar substance², right towards higher N_{BuOOH} values and when employing concentrated hydroperoxide, the maximum is observed at molar t-BuOOH/ $\text{Co}(\text{II})$ ratio being 10. Unlike this, when hydroperoxide of various concentrations is added into the $\text{Co}(\text{acac})_2$ solution, the radicals may be observed for the mole fraction N_{BuOOH} as low as 0.33. When mixing $[\text{Co}(\text{acac})_2\text{OH}]_2$ with hydroperoxide, we observed in benzene solutions a short-term formation of fairly high level of BuO_2^{\cdot} radicals, which, however, decreases rapidly with time and sets within about one minute at a stationary concentration and at room temperature.

Reaction of Tert-butyl Hydroperoxide with Cobaltous Acetylacetonate at Higher Temperatures

Hydroperoxide is well-known to be a thermally relatively stable compound² with the decomposition half-time of 10 hours at 172°C . If mixture of hydroperoxide with $\text{Co}(\text{acac})_2$ in molar ratio of 2 : 1 is heated to 75°C (30 min), all hydroperoxide is

decomposed, and if further amount of $\text{Co}(\text{acac})_2$ is added to the cooled solution, any oxidation no longer takes place (Fig. 9). Even reaction (B), involving catalytic redox cycle, took therefore place under these conditions. On heating $[\text{Co}(\text{acac})_2\text{OH}]_2$ to 80°C (60 min), the substance can be no more extracted with water or 1M hydrochloric acid from tetrachloromethane solution. Changes in number of lines of the NMR spectra show that heating provided structural changes. The original dimer is *cis*-isomer¹³, which changes into *trans*-isomer at higher temperatures.

In the infrared spectra, band 530 cm^{-1} as well as that of valency OH vibrations in region $3500\text{--}3600\text{ cm}^{-1}$ (Fig. 7, curve 4) disappears by thermal decomposition of $[\text{Co}(\text{acac})_2\text{OH}]_2$ (80°C , 20 min). The new spectrum is characteristic for the Co(III) compounds. Also the heating of reaction products of hydroperoxide with $\text{Co}(\text{acac})_2$ (1 : 2, Fig. 7, curve 7) provides equal change. We can find analogous spectrum, which may be observed in thermal decomposition of $[\text{Co}(\text{acac})_2\text{OH}]_2$, also for products of oxidation of $\text{Co}(\text{acac})_2$ with air oxygen (Fig. 7, curve 5).

Reaction of Di-*tert*-butylperoxalate with Cobaltous Acetylacetonate

In the reaction of peroxalate with $\text{Co}(\text{acac})_2$, all the cobalt present is oxidized at molar Co(II) peroxalate ratio equal to 2. In the point of equivalence, maximum d.c. con-

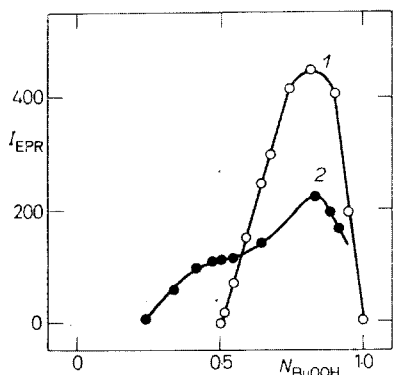


FIG. 8

Plot of Concentration of $t\text{-BuO}_2$ Radicals (expressed in terms of intensity of EPR signals) against Mole Fraction of *tert*-Butyl Peroxide in Binary Mixture

1 Titration of $t\text{-BuOOH}$ solution (10^{-1} mol/l) by the $\text{Co}(\text{acac})_2$ solution ($5 \cdot 10^{-2}$ mol/l); 2 after inverse mixing.

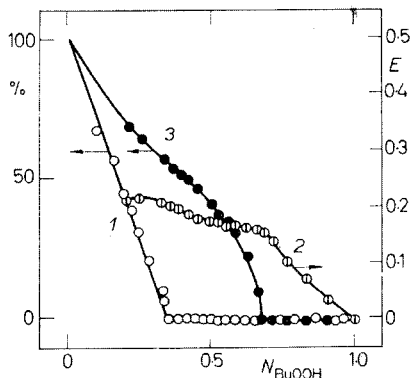
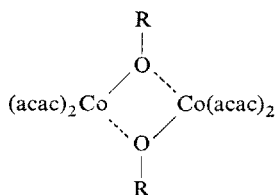


FIG. 9

Plot of Amount of Nonreacted Cobalt Acetylacetonate (1, 3) and of Extinction E_{596} (2) against Mole Fraction N_{BuOOH}

1 (Fig. 2); 2, 3 for $N_{\text{BuOOH}} = 0.66$ the system was warmed up to 80°C (60 min), experimental conditions the same as in Fig. 1 and 2.

ductivity is observed (Fig. 10). In infrared spectra the doublet band of 535 and 563 cm^{-1} in the titrated mixture (on distilling off the liquid phase) suggests formation of dimer



(Fig. 7, curve 8). Also in this case, the dimer structure is destroyed on heating, and the spectrum (Fig. 7, curve 9) is similar to spectra of the oxidized products (curves 4, 5, and 7).

Peroxalate is a thermally unstable peroxide¹⁶⁻¹⁸ and tert-butyl alcohol, tert-butyl peroxide, acetone, and CO_2 (Fig. 11) are products of its decomposition. Fig. 12 shows kinetics of thermal decomposition of peroxalate, studied by the NMR method. At room temperature and for molar Co(II) peroxalate ratio being two, the decomposition of peroxalate proceeds within 1 to 3 minutes.

Reaction of Benzoyl Peroxide with Cobaltous Acetylacetonate

In the reaction of benzoyl peroxide with Co(acac)_2 , the end of oxidation of Co(II) to Co(III) was observed only for stoichiometric Co(II) benzoyl peroxide ratio equal to 2. In this case (tetrachloromethane solution) no distinct changes in electric conductivity were found. The reaction is very slow and analysis was therefore made as late as 24 hours after attaining the stationary state.

In the infrared spectra of the reaction products of benzoyl peroxide with cobaltous acetylacetonate (1 : 4) a doublet band characteristic for dimer-cyclic structures was observed; however, the band is shifted towards lower wave-numbers $488 - 514\text{ cm}^{-1}$ (Fig. 7, curve 10). Equally as in preceding experiments the characteristic doublet band vanishes on heating the sample (Fig. 8, curve 11).

When analysing the NMR spectra it was found that stepwise addition of Co(acac)_2 into the benzoyl peroxide solution provides another ratio of final products than if mixing in an opposite order is carried out (Fig. 13). If the ratio Co(II) /benzoyl peroxide is equal to 2, whereas the NMR spectra suggest a relatively high concentration of

Co(III) in the system (CH_3 protons: $\delta^1 = 2.04$, $\delta^2 = 2.00$, $\delta^3 = 2.2$; $=\text{CH}$ protons: $\delta^1 = 5.25$, $\delta^2 = 5.40$ p.p.m.), the protons of the phenyl nucleus are shifted, which could be accounted for the formation of a benzoate (or phenyl) ion bound in a complex linkage to cobalt. Analysis of shifted bands is made difficult because a greater number of them is observed than it would correspond to the five types of protons considered.

Steric isomers are here likely involved. At room temperature, decomposition of the Co(II)-complex leads to the formation of two steric isomers of associate $(\text{acac})_2\text{Co} \cdot \text{OCOPh}$. Bands δ_{CH_3} 2.04 p.p.m. and δ_{CH} 5.24 p.p.m. are assigned to *trans*-isomer, whereas bands $\delta_{\text{CH}_3}^1$ 2.01, $\delta_{\text{CH}_3}^2$ 2.29, and δ_{CH} 5.40 p.p.m. are ascribed to the *cis*-isomer.

In the reaction of $\text{Co}(\text{acac})_2$ with benzoyl peroxide, no free radicals of such a high concentration level were produced that should be detected by the EPR method.

DISCUSSION

The decomposition of hydroperoxide by cobaltous acetylacetonate in a nonpolar medium is at room temperature a stoichiometric reaction, because the primary product may produce a relatively stable dimer. Only at temperatures higher than 50°C, the reaction is obviously of the chain character, *i.e.* both reactions (A) and (B) of the redox cycle are involved. For such catalytic decomposition of hydroperoxide it is not possible to detect directly free radicals by the EPR method.

Reaction (A) is slow in polar medium, since formation of complex $[(\text{acac})_2\text{Co}] \cdot [\text{ROOH}]_n$ is more difficult. Richardson¹⁹ spectroscopically confirmed existence of complexes with hydroperoxide for copper 2-ethyl-hexanoate reacting more slowly.

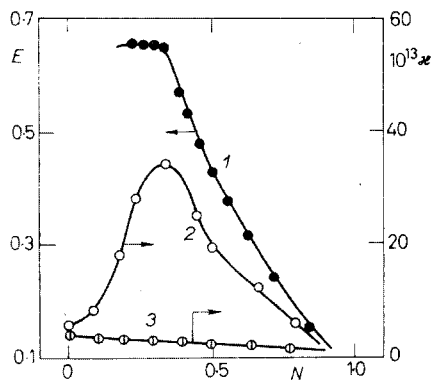


FIG. 10

Plot of Extinction E_{596} and D.C. Conductivity ($\Omega^{-1} \text{cm}^{-1}$) against Mole Fraction of Tert-butyl Peroxalate (N)

1, 2 Binary mixture with $\text{Co}(\text{acac})_2$;
3 with $\text{Co}(\text{acac})_3$; titration of peroxalate solution ($8 \cdot 10^{-3} \text{ mol/l}$) by $\text{Co}(\text{acac})_2$ solution ($3 \cdot 10^{-2} \text{ mol/l}$) at room temperature.

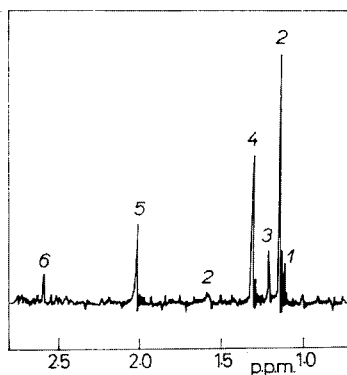


FIG. 11

NMR Spectra of Products of Thermal Decomposition of Di-tert-butyl Peroxalate

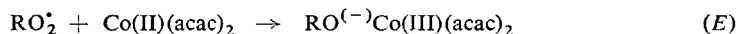
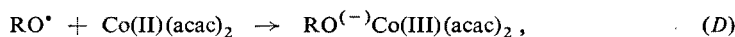
1 Tert-butyl peroxide, 2 tert-butyl alcohol, 4 peroxalate, 5 acetone, 3, 6 nonidentified products.

Changes connected with liberation of coordination places have a decisive significance for reactions in the coordination sphere of transition metals. Primary products of the redox step are radicals RO^{\bullet} which under suitable reaction conditions may be taken up in the coordination sphere of Co(III). For tertiary butyl hydroperoxide, however, the RO_2^{\bullet} radicals^{10,11} only were always found by the EPR method, which are apparently product of fast reaction²⁰



which proceeds in outer coordination sphere of cobalt.

Diamagnetic products of fast reactions⁹ of radicals with Co(II)



are electrically more conductive than substances inferring the reaction. On addition

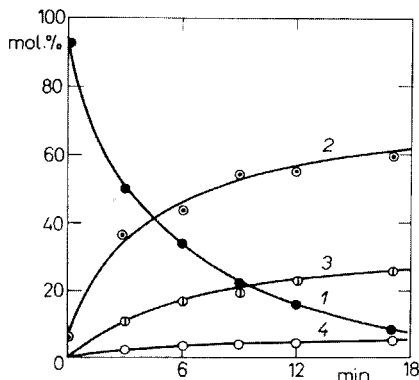


FIG. 12

Thermal Decomposition of Di-tert-butyl Peroxalate with Time, Indicated by Change in Intensity of Bands in NMR Spectra (Relative Change of the Concentration of Components in mol %)

1 Peroxalate of starting concentration 0.1 mol/l in tetrachloromethane; 2 tert-butyl alcohol; 3 acetone; 4 tert-butyl peroxide; temperature of 60°C.

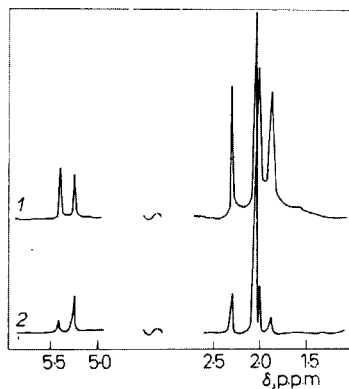
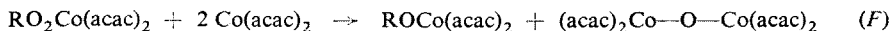


FIG. 13

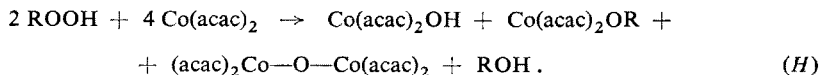
NMR Spectra of Benzoyl Peroxide in Reaction with Cobaltous Acetylacetonate in Equimolar Ratio and for Different Way of Mixing

1 $Co(acac)_2$ added into benzoyl peroxide, 2 benzoyl peroxide added into $Co(acac)_2$; tetrachloromethane concentration of 0.2 mol/l.

of further amount of $\text{Co}(\text{acac})_2$, the reaction (E) product probably further decomposes according to



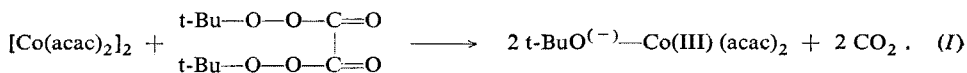
so that summary stoichiometric reaction (A), (C), (E), (F), after the titration had been finished, may be formulated in the following way



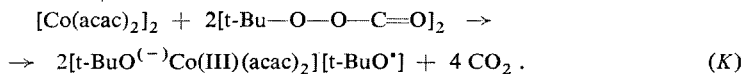
Only after exceeding molar ratio $\text{BuOOH}/\text{Co}(\text{II}) = 0.5$, when the cobalt present is mostly in the oxidized form $\text{Co}(\text{III})$, radicals with the prolonged life-time may be observed by the EPR method; their level rises with excessive BuOOH . The still increasing level of radicals cannot be interpreted as a phenomenon determined kinetically²¹. The concentration of radicals is gradually summed up. Every point requires during titration a certain time interval, within which reactive free radicals would be extinguished more rapidly than if further amount of peroxide is added.

The life-time of radicals is considerably shorter, when generation of them proceeds in reaction (B). In that case we observe "free" RO_2^{\bullet} radicals, a majority of them being destroyed by recombination or in reaction (E). During recombination oxygen is evolved which is responsible for broadening of lines in the NMR spectra and which itself can be coordinated in the coordination sphere of cobalt complexes $2 \text{RO}_2^{\bullet} \rightarrow \text{ROOR} + \text{O}_2$.

For di-tert-butyl peroxalate the summary reaction, which is completed at molar ratio $\text{Co}(\text{II})$ peroxalate = 2, can be interpreted by

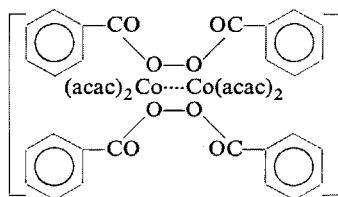


The maximum of BuO^{\bullet} radicals was observed¹² for equimolar $\text{Co}(\text{II})/\text{BuOOH}$ ratio, which corresponds to reaction



For benzoyl peroxide, even if the redox step is realized, no EPR signals are observed. We assume that the electron transfer between $\text{Co}(\text{II})$ and the $-\text{O}-\text{O}-$ bond proceeds as a virtually two-electron one without any symmetry of primary associate

between $[\text{Co}(\text{acac})_2]_2$ and benzoyl peroxide being destroyed



All protons in the CH_3 -groups of the ligand are equally shielded, which becomes in the EPR spectrum evident by only one $\delta_{\text{CH}_3} = 1.89$ p.p.m. band. Intensity of this band decreases with time at a speed at which the complex decomposes under simultaneous formation of new bands $\delta_{\text{CH}_3}^1$ 2.04, $\delta_{\text{CH}_3}^2$ 2.01, and $\delta_{\text{CH}_3}^3$ 2.29 p.p.m., belonging to final products of the cobalt oxidation.

Tertiary butyl peroxide does not react with cobaltous acetylacetonate at the temperature as high as 60°C , probably due to the fact that voluminous tertiary butyl groups sterically prevent formation of the associate of peroxide with $[\text{Co}(\text{acac})_2]_2$.

REFERENCES

1. Denisov E. T.: *Uspechi Chim.* 40, 43 (1971).
2. Swern D. (Ed.) in the book: *Organic Peroxides*, Vol. 1, Vol. 2. Wiley, New York 1970.
3. Dean M. H., Skirrow G.: *Trans. Faraday Soc.* 54, 849 (1958).
4. Richardson W. H.: *J. Am. Chem. Soc.* 87, 1096 (1965).
5. Scott E. J. Y.: *J. Phys. Chem.* 74, 1174 (1970).
6. Osawa Z., Shibamiya T., Ogiwara Y., Matsukoki K.: *Kogyo Kagaku Zasshi* 73, 115 (1970); *Chem. Abstr.* 73, 110210.
7. Richardson W. H.: *J. Am. Chem. Soc.* 87, 247 (1965).
8. Bulgakova G. M., Skobida I. P., Majzus Z. K.: *Kinetika i Kataliz* 12, 76 (1971).
9. Ščeredin V. P., Denisov E. T.: *Izv. Akad. Nauk SSSR* 1967, 1428.
10. Brandon R. W., Elliot C. S.: *Tetrahedron Lett.* 1967, 4375.
11. Tkáč A., Veselý K., Omelka L.: *J. Phys. Chem.* 75, 2575, 2580 (1971).
12. Tkáč A., Veselý K., Omelka L.: *This Journal*, in press.
13. Boucher L. J., Herrington D. R.: *J. Inorg. Nucl. Chem.* 33, 4349 (1971).
14. Přikryl R., Tkáč A., Staško A.: *This Journal* 37, 1295 (1972).
15. Nakamoto K. in the book: *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley, New York 1963.
16. Bartlett P. D., Benzing E. P., Pincock R. E.: *J. Am. Chem. Soc.* 82, 1762 (1964).
17. Hiatt R., Traylor T. G.: *J. Am. Chem. Soc.* 87, 3766 (1965).
18. Mayo F. R.: *Intra. Sci. Chem. Rev.* 3, 277 (1963).
19. Richardson W. H.: *J. Am. Chem. Soc.* 88, 975 (1966).
20. Hiatt R., Clipsham J., Visser T.: *Can. J. Chem.* 42, 2754 (1964).
21. Ingold K. U.: *J. Phys. Chem.* 76, 1385 (1972).

Translated by J. Hejduk.