

## COMPLEX BONDED ALKOXY RADICALS\*

A. TKÁČ<sup>a</sup>, K. VESELÝ<sup>b</sup> and L. OMELKA<sup>a</sup><sup>a</sup>*Institute of Chemical Physics, Department of Physical Chemistry,  
Slovak Technical University, 880 37 Bratislava,*<sup>b</sup>*Research Institute of Macromolecular Chemistry, 600 00 Brno*

Received June 4th, 1973

At the reaction of tert-butyl peroxalate with Co(II)-acetylacetonate in nonpolar solvents (benzene, toluene, hexane, tetrachloromethane) and in an inert atmosphere (nitrogen, argon) a ESR signal-singlet ( $g = 2.0058 \pm 0.0003$ ) is generated. The intensity of the signal depends on the molar ratio of the components. At room temperature, the signal is observable for several hours and is assigned to a complex of t-BuO<sup>•</sup> radicals with Co(III). On mixing of Co(acac)<sub>2</sub> solution, which was at lower temperature saturated with oxygen, with peroxalate a broad signal having  $g = 2.0153 \pm 0.0004$  is formed which, at room temperature, quickly transforms to a narrow singlet ( $g = 2.0058$ ). It is assumed that at the reaction of peroxalate with diamagnetic complex L<sub>2</sub>CoO<sub>2</sub> · CoL<sub>2</sub> the t-BuO<sub>3</sub><sup>•</sup> radicals are formed which decompose above 10°C to give t-BuO<sup>•</sup> radicals and oxygen. Peroxalate in benzene solution when exposed to light and in the presence of oxygen decomposes to give acetone and reactive CH<sub>3</sub><sup>•</sup> radicals; the solvent undergoes simultaneous oxidation. This system reacts with Co(acac)<sub>2</sub> to give paramagnetic complex Co(III) with phenoxy radicals, or a complex Co(II) with semiquinone radicals. ESR signals of such cobalt containing complexes are octets ( $g = 1.9998 \pm 0.0003$ ,  $a_{Co} = 10$  Oe), which are highly stable at room temperature.

Bartlett and coworkers<sup>1</sup> were the first in using tert-butyl peroxalate as a source of t-BuO<sup>•</sup> radicals. Mechanism of its thermal decomposition was studied by several authors<sup>2-6</sup>. The possibility of generation of tert-butoxy radicals at the reaction of peroxalate in the presence of Co(acac)<sub>2</sub> has already been quoted in our previous communication<sup>7</sup>, but up to now, the problem has not been quantitatively analysed and also the subsequent reactions with oxygen have not yet been described. The present study compares the reactivity of RO<sup>•</sup> radicals which are complex bonded in the coordination sphere of Co(III) with the reactivity of analogous complexes of RO<sub>2</sub><sup>•</sup> radicals, and also the experimental conditions for RO<sub>3</sub><sup>•</sup> radicals formation are presented.

## EXPERIMENTAL

Preparation and purification of chemicals have been quoted in our previous study<sup>7</sup>. Tert-butyl peroxalate was prepared from tert-butyl hydroperoxide and oxalyl chloride in the presence of

\* Part III in the series Radical Reactions in the Ligand Field of Transition Metals; Part II: J. Phys. Chem. 75, 2580 (1971).

pyridine<sup>1</sup>; the product was stored at low temperature in the dark, and under hexane in an inert atmosphere. Mixtures with 2% solution of  $\text{Co}(\text{acac})_2$  were prepared either by mixing in the ESR cells (procedure 1), or in tempered vessels equipped with magnetic stirrer (procedure 2) or in an adapted ESR cell (procedure 3, Fig. 1). Freshly prepared 5% solutions of peroxalate in nonpolar solvents were concentrated by vacuum evaporation up to 50% of the initial volume in side arms of the adapted esr cells. In this way the polar products of decomposition (tert-butyl alcohol in hexane, acetone in benzene) were removed just before peroxalate came into contact with  $\text{Co}(\text{acac})_2$  (recrystallized from ethanol).  $\text{Co}(\text{acac})_2$  was dried over  $\text{P}_2\text{O}_5$  in an esr cell at  $110^\circ\text{C}/10^{-2}$  Torr (the drying vessel with  $\text{P}_2\text{O}_5$  was permanently joined with the measuring cell). Concentrated solution of peroxalate was at  $5-7^\circ\text{C}$  gradually added to  $\text{Co}(\text{acac})_2$  by tilting the cell; the mixing was accomplished by an ultrasonic generator during 10 seconds at  $10^\circ\text{C}$ . A commercial x-band spectrometer Varian E-3 equipped with 100 kHz field modulation was used.

## RESULTS

### *Reactions in an Inert Atmosphere*

When mixing freshly prepared solutions of tert-butyl peroxalate and of  $\text{Co}(\text{acac})_2$  in nonpolar solvents (hexane, tetrachloromethane, benzene, toluene) the originally violet color of  $\text{Co}(\text{acac})_2$  solutions turns green and the esr signal as a relatively narrow line-singlet, having  $g = 2.0058 \pm 0.0003$  and the line width of 2 Oe (Fig. 2) is observed. The signal intensity slowly decreases with time, but still after several hours it can be observed at the radical concentration level of  $10^{13}/0.3$  ml (room temperature, benzene solution). The smallest rate of radical disappearance is observed in tetrachloromethane. Paramagnetic properties are not lost by drying the system under vacuum.

If peroxalate solution is gradually added to a  $\text{Co}(\text{acac})_2$  solution (by using the procedure 1 or 2) the esr signal intensity reaches the maximum value of  $4 \cdot 10^{14}$  spin/0.3 ml at the molar ratio of 1 : 1 (Fig. 3). The signal is observable at the temperatures ranging from  $-150^\circ\text{C}$  to  $+90^\circ\text{C}$ ; its intensity drops down to 50% at  $-100^\circ\text{C}$ . At  $90^\circ\text{C}$  the signal intensity drop to 50% is attained after 20 min.

### *Reactions in the Presence of Oxygen*

If benzene or tetrachloromethane solution of  $\text{Co}(\text{acac})_2$  or even crystalline  $\text{Co}(\text{acac})_2$  is saturated with oxygen at  $5-6^\circ\text{C}$  (procedure 3) and then cooled peroxalate solution is added, an intensive signal, which has a bandwidth value of 20 Oe and high  $g$ -value ( $g = 2.0153 \pm 0.0004$ ) is observed in the very first moments of the reaction. The signal mentioned fades away during temperature rise to  $20^\circ\text{C}$  in the ESR cavity and a narrow singlet having  $g$ -value of 2.0058 (Fig. 4) is observed.

Tert-butyl peroxalate solution in an aromatic solvent (benzene, toluene) on exposure to light and in the presence of oxygen turns slightly yellow during two hours at room temperature. If now such a solution is let to react with  $\text{Co}(\text{acac})_2$ , either in an inert atmosphere or in the presence of oxygen, ESR signal observed is splitted into 8 lines

of practically the same intensity ( $g = 1.9998 \pm 0.0003$ , coupling constant  $a_{Co} = 10 \text{ Oe}$ ); the intensity slightly decreases toward the end lines (Fig. 5a). These octet signals are more intensive the longer time the benzene solution of peroxalate was exposed to light and oxygen at room temperature. Under the same conditions in  $\text{CCl}_4$  solution only a singlet-signal is observed. If peroxalate in benzene solution is let to decompose completely during two months and the yellow component (which is paramagnetic, singlet  $g = 2.0038 \pm 0.0003$ , linewidth 6 Oe) is isolated and then added to  $\text{Co}(\text{acac})_2$ , an octet with equal intensities of all lines is observed. In this case, the oxidation  $\text{Co}(\text{II}) \rightarrow \text{Co}(\text{III})$  does not take place and  $\text{Co}(\text{acac})_2$  solution stays rose after mixing of the reactants.

Under suitable spectroscopis conditions (low concentration, solution free of molecular oxygen) each line of the octet splits into a doublet ( $a_H = 5 \text{ Oe}$ , Fig. 5b). With increasing temperature the intensity of the octet signal decreases and at  $90^\circ\text{C}$  only a single line having  $g = 2.0058$  (Fig. 5c) is recorded. This phenomenon is possible only with such octet ESR signals which have middle lines of higher intensity, this indicates the superposition of two signals: an octet and a singlet which have different sensitivity towards temperature rise.

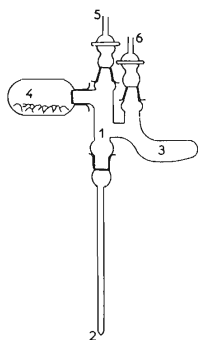


FIG. 1  
ESR Cell for Successive Mixing of Reactants under Inert Atmosphere (Procedure 3)

1 Reaction vessel, 2 measuring tube of ESR cell, 3 side vessel with peroxalate, 4 drying vessel with  $\text{P}_2\text{O}_5$ , 5, 6 three-way taps.

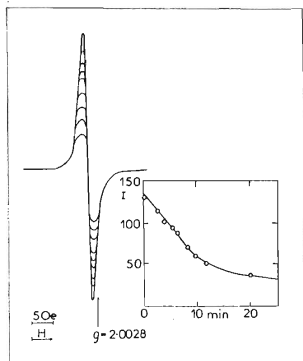


FIG. 2  
ESR Signal of  $t\text{-BuO}\cdot$  Radicals and its Variation with Time at  $23^\circ\text{C}$

Benzene solutions, inert atmosphere, reaction of  $\text{Co}(\text{acac})_2 + \text{tert-butyl peroxalate}$  performed according to procedure 1.

That the octet  $\rightarrow$  singlet transformation is not due to an irreversible evolution of molecular oxygen from a complex with cobalt, can be confirmed by the following facts: neither the single-line signal generated under a nitrogen atmosphere can be transformed to an octet, even if the oxygen pressure of 3 atm is applied, nor the octet signal can be transformed to the single-line ESR signal by bubbling nitrogen through the reaction solution.

#### *Radical Generation in the System Tert-Butyl Peroxalate-Tert-Butyl Hydroperoxide*

At the reaction of  $\text{Co}(\text{acac})_2$  with equimolar mixture of peroxalate and hydroperoxide only one signal assigned to a complex bonded  $t\text{-BuO}_2^{\bullet}$  radicals to a cobalt atom (broad singlet having high  $g$ -value 2.0147) is observed. Similarly, if hydroperoxide is added to a system with  $\text{RO}^{\bullet}$  radicals, the original esr signal disappears and instead a signal, which is characteristic for  $\text{RO}_2^{\bullet}$  radicals, is observed.

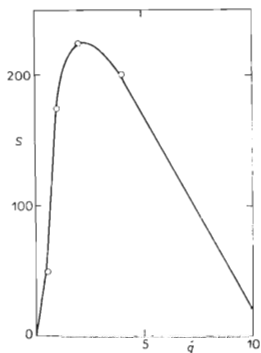


FIG. 3

Area of ESR Signal of Complex Bonded  $t\text{-BuO}^{\bullet}$  Radicals versus Molar Ratio tert-Butyl Peroxalate/ $\text{Co}(\text{acac})_2$  ( $q$ )

Prepared according to procedure 2 under inert atmosphere in benzene solution at room temperature (peroxalate-10% solution,  $\text{Co}(\text{acac})_2$ -2% solution).

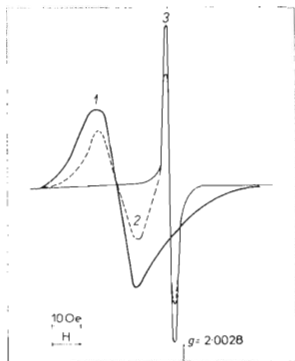


FIG. 4

Transformation of ESR Signal of  $t\text{-BuO}_2^{\bullet}$  to the Signal of  $t\text{-BuO}^{\bullet}$  in Oxygen Atmosphere at Room Temperature

1 Immediately after mixing of reactants at  $5^{\circ}\text{C}$ , 2 after 5 minutes at  $23^{\circ}\text{C}$ , 3 after 10 minutes;  $\text{Co}(\text{acac})_2$  solution (or crystalline) saturated with dried oxygen according to procedure 3 before the reaction.

### Displacement of Radicals from the Complex

The intensity of singlet as well as octet signals is decreased by the presence of polar compounds (water, methanol, ethanol). At the molar ratio ethanol/peroxalate of 10, the intensity drops by as much as 80% (Fig. 5). The displacement of RO' radicals from the complexes with Co(III) by polar compound is less efficient as in case of complexes of RO<sub>2</sub>' radicals<sup>26</sup>.

### Reactivity of [Co]t-BuO' Complexes

Krajlic and Trumbore<sup>8</sup> have found *p*-nitroso-*N*-dimethylaniline to be an efficient scavenger of HO' radicals. Both singlet and octet signals of RO' complexes are im-

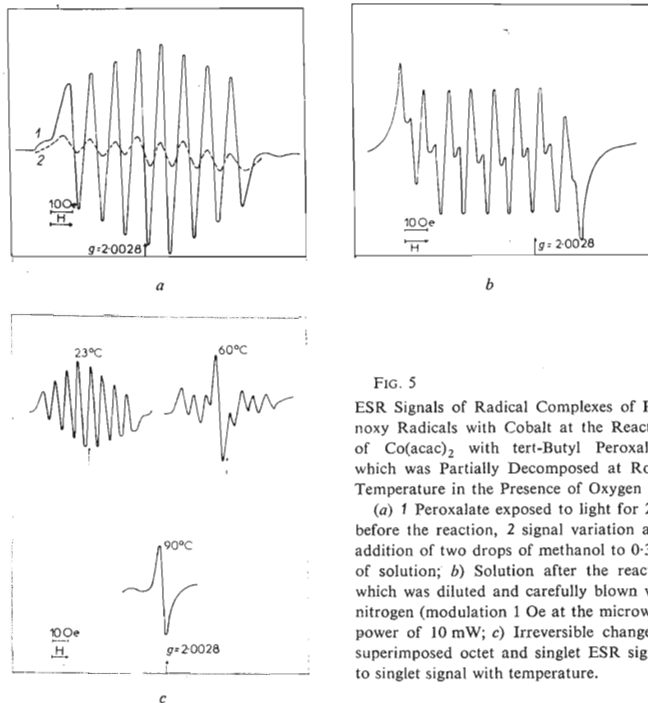


FIG. 5

ESR Signals of Radical Complexes of Phenoxy Radicals with Cobalt at the Reaction of Co(acac)<sub>2</sub> with *tert*-Butyl Peroxalate, which was Partially Decomposed at Room Temperature in the Presence of Oxygen

(a) 1 Peroxalate exposed to light for 24 h before the reaction, 2 signal variation after addition of two drops of methanol to 0.3 ml of solution; b) Solution after the reaction which was diluted and carefully blown with nitrogen (modulation 1 Oe at the microwave power of 10 mW); c) Irreversible change of superimposed octet and singlet ESR signals to singlet signal with temperature.

mediately transformed to a new esr signal – triplet, if the complexes are brought into contact with the compound mentioned. The triplet signal has equal intensity of all three lines which is characteristic for an interaction of an unpaired electron with a magnetic moment of nitrogen nucleus ( $I = 1$ , Fig. 6a). Butoxy radicals react with phenols to give stabile “free” or complex bonded phenoxy radicals, *e.g.* by interaction with 2,6-di-*tert*-butyl-4-(1-phenylethyl)phenol a new signal-doublet, which is further splitted into a 1 : 2 : 1 triplet ( $a_{H,para} = 7$  Oe,  $a_{H,meta} = 1.75$  Oe) is observed, whereas the interaction with 2,4,6-tri-*tert*-butylphenol leads to a triplet 1 : 2 : 1 ( $g = 2.0060 \pm 0.0003$ ,  $a_{H,meta} = 1.8$  Oe). At the reaction of 2,6-di-*tert*-butyl-4-methylphenol with *t*-BuO<sup>•</sup> radicals a quartet 1 : 2 : 2 : 1 appears, which is further splitted into a triplet 1 : 2 : 1. Unpaired electron of phenoxy radical interacts with three equal protons of methyl group and with two *meta* positioned protons of benzene nucleus (Fig. 6b). Phenols, which have at least one *ortho* position unsubstituted, form phenoxy radicals which are complex bonded with cobalt. The interaction of an unpaired

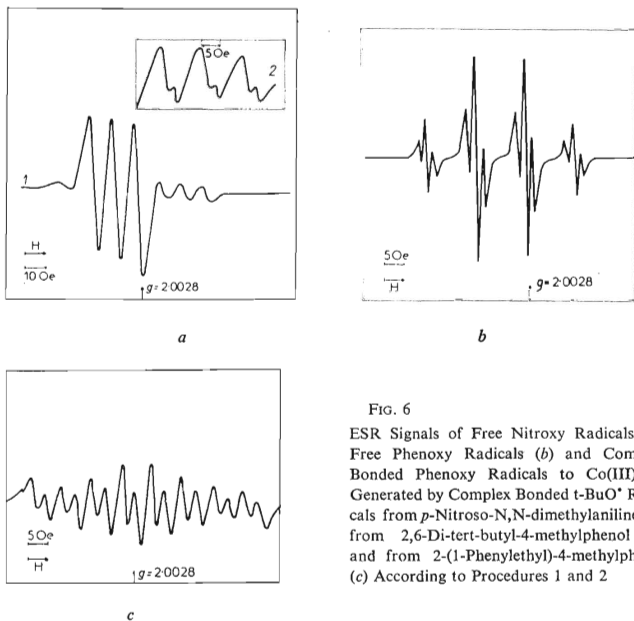


FIG. 6  
ESR Signals of Free Nitroxy Radicals (a), Free Phenoxy Radicals (b) and Complex Bonded Phenoxy Radicals to Co(III) (c) Generated by Complex Bonded *t*-BuO<sup>•</sup> Radicals from *p*-Nitroso-*N,N*-dimethylaniline (a), from 2,6-Di-*tert*-butyl-4-methylphenol (b) and from 2-(1-Phenylethyl)-4-methylphenol (c) According to Procedures 1 and 2

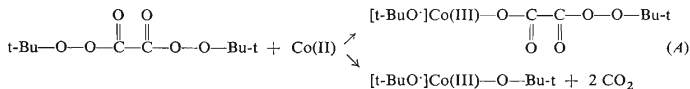
electron with a magnetic moment of the nucleus ( $I = 7/2$ ) gives an octet signal, which is further splitted by other protons of the benzene ring. As an example of such a ESR signal can serve the spectrum in Fig. 6c, which is obtained by interaction of  $\text{RO}^\bullet$  radicals with 2-(1-phenylethyl)-4-methylphenol.

### Microwave Power

The ESR spectra of cobalt-radical complexes cannot be saturated even if the power of 240 mW is applied.

### DISCUSSION

ESR signals of complex bonded peroxy radicals<sup>7</sup> can be unambiguously distinguished from complex bonded alkoxy radicals by knowing the  $g$ -values ( $\text{t-BuO}_2^\bullet$ ,  $g = 2.0147$ ;  $\text{t-BuO}^\bullet$ ,  $g = 2.0058$ ). In contrast to  $\text{RO}_2^\bullet$  radicals the complex bonded  $\text{RO}^\bullet$  radicals have  $g$ -value slightly higher than free  $\text{t-BuO}^\bullet$  radicals prepared by photolysis of di-tert-butyl peroxide ( $g = 2.0040 \pm 0.0004$ )<sup>9</sup>. The high value of  $\text{RO}_2^\bullet$  radicals has been explained by Thomas<sup>10</sup> by spin-orbital relaxation mechanism at not completely quenched orbital magnetic moment of the outer rotating oxygen atom with unpaired electron  $\text{R}-\text{O}-\text{O}^\bullet$ . Coordination through nonbonding electron pair of inner oxygen atom satisfactorily explains equal  $g$ -values of complex bonded and free  $\text{RO}_2^\bullet$  radicals in contrast to  $\text{RO}^\bullet$  radicals. We assume, that in an inert medium, the coordination of  $\text{t-BuO}^\bullet$  radicals, after the peroxide bond is broken, proceeds according to the following scheme:



The coordination sphere of cobalt nucleus by forming 18-electron valency configuration increases the stability of complex bonded  $\text{t-BuO}^\bullet$  radicals much more than in case of  $\text{t-BuO}_2^\bullet$  radicals. Their reactivity with phenols and arylamines is high and in the presence of tert-butyl hydroperoxide the induced decomposition:  $\text{RO}^\bullet + \text{ROOH} \rightarrow \text{ROH} + \text{ROO}^\bullet$  takes place and therefore only ESR signal of  $\text{RO}_2^\bullet$  radicals is observed.

In contrast to the complex bonded  $\text{t-BuO}^\bullet$  radicals, the complex bonded  $\text{t-BuO}_2^\bullet$  radicals form diamagnetic tetroxides<sup>7</sup>, if the temperature is lowered below  $0^\circ\text{C}$ . These are more stable than tetroxides formed from free  $\text{RO}_2^\bullet$  radicals which were observed at very low temperatures by Bennet and coworkers<sup>11</sup>.

The reduction of peroxalate  $\text{O}-\text{O}$  bond by  $\text{Co}(\text{acac})_2$  in nonpolar solvents saturated with oxygen at lowered temperature, in contrast to tert-butyl hydroperoxide,

leads to an unstable broad singlet with high  $g$  value ( $g = 2.0153 \pm 0.0004$ ) and spectroscopic parameters analogous to the signal of  $t\text{-BuO}_2^{\cdot}$  radicals ( $g = 2.0147 \pm 0.0003$ ). But the properties of both signals basically differ with the change of temperature. If the temperature is lowered, the new type of signal does not cease, tetroxides are not formed and above  $10^\circ\text{C}$  the signal irreversibly disappears and a new narrow line corresponding to  $t\text{-BuO}^{\cdot}$  radicals is generated ( $g = 2.0058 \pm 0.0003$ ). Considering the fact that  $t\text{-BuO}_2^{\cdot}$  radicals can not be formed in the

TABLE I  
EPR Spectroscopic Parameters of Cobalt Complexes with Oxygen and Phenoxy Radicals

Medium	$T, ^\circ\text{C}$	$g$ -Factor			$a_{\text{Co}}, \text{Oe}$			Ref.
		$\parallel$	$\perp$	iso	$\parallel$	$\perp$	iso	
[Co-tetrakis( <i>p</i> -methoxyphenyl)porphyrine]-pyridine-oxygen								
Toluene	-196	2.002	2.077	—	16	10	—	14
[N,N'-Ethylenebis(salicylaldiminato)Co]-oxygen								
Pyridine	-37	—	—	2.023	—	—	12.9	15
Pyridine	-35	—	—	2.023	—	—	12.8	15
4-Methylpyridine	20	—	—	2.022	—	—	13	15
[N,N'-Ethylenebis(3-methoxysalicylidiminato)Co]-oxygen								
Toluene-PPh <sub>3</sub>	-35	—	—	2.024	—	—	15.3	15
Dimethyl sulfoxide	20	—	—	2.028	—	—	17.3	15
Hexamethylphosphor- triamide	20	—	—	2.022	—	—	19.0	15
[Bis(dimethylglyoxime)Co]-oxygen								
Benzene-pyridine	-173	2.000	2.065	—	—	—	—	16
Benzene-pyridine	25	—	—	2.030	—	—	15	16
Vitamin B <sub>12r</sub> -oxygen								
Methanol	-196	2.004	2.070	—	11	14	—	17
Co[CH <sub>3</sub> -C(O) <sup>(-)</sup> =CH(CH <sub>3</sub> )=NCH <sub>2</sub> ] <sub>2</sub> -oxygen								
Toluene-pyridine	-74	—	—	2.0263	—	—	13.7	18
Co(acac) <sub>2</sub> -product of di-tert-butyl peroxalate								
Benzene	-150 to 40	—	—	1.9998	—	—	10	this work



absence of hydroperoxide and, furthermore, that  $\text{Co}(\text{acac})_2$  solution saturated with oxygen forms diamagnetic  $\text{L}_2\text{Co}-\text{O}-\text{O}-\text{CoL}_2$  complexes<sup>12</sup>, we may suppose an intermediate formation of "ozonide radical"  $t\text{-BuO}_3^{\cdot}$  whose existence has already been postulated by Symonson<sup>13</sup> as an intermediate product of hydroperoxide photolysis. Orbital contribution of rotating outer oxygen can be slightly higher than in case of  $t\text{-BuO}_2^{\cdot}$  radicals. At the temperatures higher than  $5^\circ\text{C}$   $t\text{-BuO}_3^{\cdot}$  radical irreversibly decomposes to  $t\text{-BuO}^{\cdot}$  radical and molecular oxygen.

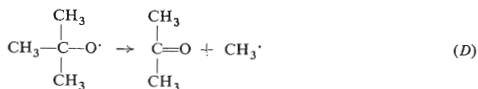


The explanation of the formation of octet signals in the presence of oxygen only in aromatic solvents is rather complicated problem. One can exclude the possibility that the octet signal is due to the paramagnetism of  $\text{Co}(\text{II})$  monomer with unpaired  $3d^7$  electron. ESR spectra of cobalt complexes have been recorded only at extremely low temperatures in crystalline phase<sup>14</sup>. Two superimposed octets with anisotropic  $g$ -value have been observed; *e.g.* for tetrakis(*p*-methoxyphenyl)porphyrine- $\text{Co}(\text{II})$   $g_{\perp} = 3.285$  and  $g_{\parallel} = 1.79$ ; the coupling constant  $a_{\text{Co}}$  400 Oe in toluene solution decreased to 200 Oe. If we take these values as a measure of maximum interaction of unpaired electron with magnetic moment of cobalt nucleus, the observed value of 10 Oe indicates that up to 95% of electron spin density is localised on oxygen atom. The value of  $g$  and of coupling constant of the reaction products of cobalt complexes and oxygen which were interpreted<sup>15-18</sup> as superoxides  $\text{Co}(\text{III})\text{O}_2^-$  are summarized in Table I.

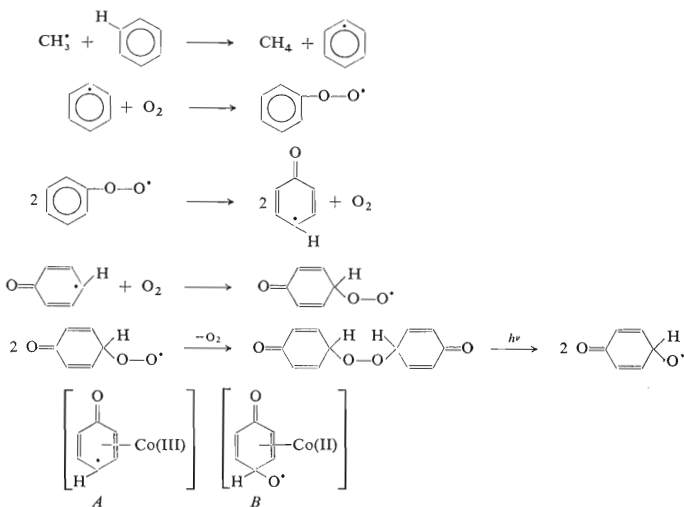
Experimental results indicate that the octet signals belong to paramagnetic complexes of benzene and toluene oxidation products with cobalt. Several authors<sup>19-23</sup> have quoted that aromatic compounds can be transformed to phenols in the presence of peroxides and metals. Hiatt<sup>20</sup> describes the formation of phenol from benzene in the presence of oxygen and tert-butyl hydroperoxide. Retardation of certain auto-oxidation reactions in benzene solutions has also been explained by the formation of phenols<sup>22</sup>. The elementary reaction step assumes the formation of alkyl-radical-aromatic complexes<sup>23</sup>, which then react with molecular oxygen to give phenol and water:



Phenols can also be formed by abstraction of hydrogen from an aromatic ring by an alkyl radical<sup>24</sup>. Methyl radicals are secondary products of thermal decomposition of tert-butyl peroxalate, even at room temperature. Primary tert-butoxy radicals formed in nonpolar solvents, if they are not stabilised by hydrogen abstraction to form tert-butyl alcohol, decompose to give acetone and  $\text{CH}_3^{\cdot}$  radicals<sup>2-5</sup>



The formation of semiquinones and phenoxy radicals is clarified by the reaction Scheme 1. The octet ESR signals observed in rose solutions of  $\text{Co}(\text{acac})_2$  after the



SCHEME 1

addition of oxidatively decomposed peroxalate in benzene and exposed to light (yellow colour due to the presence of semiquinones) is assigned to complexes of unoxidized cobalt  $\text{Co}(\text{II})$  with semiquinones (type *B*, Scheme 1), whereas the green solutions of  $\text{Co}(\text{acac})_2$  obtained by the addition of slightly (in the dark) decomposed peroxalate in oxygen atmosphere, to the complexes of oxidized cobalt  $\text{Co}(\text{III})$  with phenoxy radicals (type *A*, Scheme 1). The complexes of  $\text{Co}(\text{II})$  with free nitroxy radicals have recently been published by Brown and coworkers<sup>25</sup> and with stable 2,4,6-tri-*tert*-butylphenoxy radicals have been quoted in our previous communication<sup>26</sup>. The splitting of octets, due to the interaction of unpaired electron with one dominating proton in para position, to give 16-line spectrum is probable with both types of complexes quoted, but it was proved for the type *A* (Fig. 6c). By rising the

temperature, the cobalt complexes irreversibly decompose and the radicals formed cease by subsequent reactions. In case that superimposed signals of the octet complexes and the complex bonded t-BuO<sup>•</sup> radicals are observed, the temperature rise over 40°C leads to the disappearance of the octet signals and the singlet of the complex bonded t-BuO<sup>•</sup> radicals stays unchanged.

The complex bonded tert-butoxy radicals, similarly as tert-butylperoxy radicals<sup>26-28</sup>, are highly reactive, even at room temperature, and generate from phenols and from arylamines (as well as from *p*-nitroso-N,N-dimethylaniline) either free or to cobalt complex bonded radicals.

*The authors' thanks are due to Dr M. Uhliř, Research Institute of Macromolecular Chemistry, Brno, for the preparation of high purity di-tert-butyl peroxalate used in this study.*

#### REFERENCES

1. Bartlett P. D., Benzing E. P., Pincock R. E.: *J. Am. Chem. Soc.* **82**, 1762 (1960).
2. Bartlett P. D., Gunther P.: *J. Am. Chem. Soc.* **88**, 3288 (1966).
3. Hiatt R., Traylor T. G.: *J. Am. Chem. Soc.* **87**, 3766 (1965).
4. Kiefer H., Traylor T. G.: *J. Am. Chem. Soc.* **89**, 6667 (1967).
5. Mayo F. R.: *Intra-Sci. Chem. Rep.* **3**, 277 (1969).
6. Sheldon R. A., Kochi J. K.: *J. Org. Chem.* **35**, 1223 (1970).
7. Tkáč A., Veselý K., Omelka L.: *J. Phys. Chem.* **75**, 2575 (1971).
8. Krajič I., Trumbore C. N.: *J. Am. Chem. Soc.* **87**, 2547 (1965).
9. Weiner S., Hammond G. S.: *J. Am. Chem. Soc.* **91**, 2182 (1969).
10. Thomar J. R.: *J. Am. Chem. Soc.* **88**, 2064 (1966).
11. Bennett J. E., Brown D. J., Mile B.: *Trans. Faraday Soc.* **66**, 397 (1970).
12. Munakata M.: *Bull. Chem. Soc. Japan* **44**, 1781 (1971).
13. Symons M. C. R.: *J. Am. Chem. Soc.* **91**, 5924 (1969).
14. Walker F. A.: *J. Am. Chem. Soc.* **92**, 4235 (1970).
15. Koda S., Mison A., Uchida Y.: *Bull. Chem. Soc. Japan* **43**, 3143 (1970).
16. Schrauzer G. N., Lee L. P.: *J. Am. Chem. Soc.* **92**, 1551 (1970).
17. Bayston J. H., King N. K., Loonery F. D., Winfield M. E.: *J. Am. Chem. Soc.* **91**, 2775 (1969).
18. Hoffman B. M., Diemente D. L., Basolo F.: *J. Am. Chem. Soc.* **92**, 61 (1970).
19. Indiktor N., Jochsberg T., Kurnit D.: *J. Org. Chem.* **34**, 2861 (1969).
20. Hiatt R.: *J. Org. Chem.* **33**, 1416 (1968).
21. Kovacic P., Kurz M.: *J. Am. Chem. Soc.* **88**, 2068 (1966).
22. Ingold K. U.: *Chem. Rev.* **61**, 563 (1961).
23. Huyser E. S. in the book: *Advances in Free Radical Chemistry* (G. H. Williams, Ed.), p. 77. Logos Press, London 1965.
24. Cotrell T. L.: *The Strengths of Chemical Bonds* 2. Ed. Butterworths, London 1968.
25. Brown D. G., Maier T., Drago R.: *Inorg. Chem.* **10**, 2804 (1971).
26. Tkáč A., Veselý K., Omelka L.: *J. Phys. Chem.* **75**, 2580 (1971).
27. Tkáč A., Omelka L., Veselý K.: Preprint Vo-P-26, *International Conference on Chemical Transformation of Polymers*, Bratislava 1971.
28. Tkáč A., Omelka L., Holčík M.: Preprint D-1, *Mechanism and Inhibition Processes of Polymers*, IUPAC 11th Microsymposium, Prague 1972.