RADICAL PRODUCTS OF HYDROXYLAMINES, NITRONES AND SPIN ADDUCTS IN THE PROCESS OF GRADUAL OXIDATION WITH COORDINATED PEROXY-RADICALS*

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Hydroxyperoxides and cobalt-coordinated peroxy-radicals oxidize hydroxylamines as *e.g.* Et_2NOH, $(PhCH_2)_2NOH$, $PhCH_2PhNOH$ to the respective nitrones, and the spin adducts — nitrone and peroxy-radical — are formed. In contrast to hydroperoxides the coordinated peroxy radicals can oxidize the formed spin adduct, the methylene or methine groups next to nitrogen being converted into carbonyl groups. The radical intermediates corresponding to individual steps of the gradual oxidation have been identified by means of EPR spectra.

The dissociation energy of OH bond in hydroxylamines is generally lower than that of phenolic antioxidants by 10 to 80 kJ/mol (refs[1-3]), which causes a marked H-donor character of the former compounds. This property is successfully made use of in inhibition of radical chain mechanisms of hydrocarbon oxidation[4,5], and photochemical oxidation of NO to NO_2 in atmosphere[6]. Oxidation mechanisms of hydroxylamines attracted considerable attention[9-13] also for that reason that nitrones (as their oxidation products) are effective free radical traps[18], the nitroxyl radicals themselves being known to be also able to participate in inhibition reactions[14-15]. Peroxy[16-17] or alkoxy[18] radicals generated in decomposition of peroxides can abstract hydrogen atom from OH bond. In these reactions formation of two types of radicals was observed: the primary nitroxyl radical formed by abstraction of hydrogen from the hydroxylamino group and the secondary nitroxyl radical formed by addition of alkoxy- or peroxy-radicals to nitrone.

Quantitative study of the oxidation intermediates is made difficult by the fact that sources of thermally or photochemically generated initiation radicals are not defined. Their stationary concentration is relatively low — about 10^{-7} mol . l^{-1} at laboratory temperatures. The used initiation system of tert-butylperoxy-radicals stabilized by coordination to a transition metal[19,21] (Co^{3+}) has the advantage in that it can attack the respective H-donor at a stationary concentration higher by almost three orders of magnitude (10^{-4} mol . l^{-1}) without continuous formation of oxygen by the reaction[20] $2 ROO· \rightarrow ROOR + O_2$. Under these conditions it is possible to dose quantitatively the peroxy-radicals within a broad concentration range.

Application of the said technique of initiation of radical reactions enabled gradual oxidation of aliphatic and aromatic amines as well as their subsequent products and also enabled analysis of their structure by EPR methods. Thus the present communication complements the previous studies of inhibition mechanisms in the presence of diphenylamine where hydroxylamine was presumed to be the reaction intermediate.

EXPERIMENTAL

Reagents. Tert-butylhydroperoxide — TBHP, 93% (Fluka, Switzerland); cumenehydroperoxide — CHP, 92% was prepared by concentrating the commercial product (Lachema, Brno); tetraline hydroperoxide — THP, 94% was prepared by oxidation of tetraline. The other reagents used were synthetized according to the given literature: cobalt acetylacetonate — Co^{2+} .(acac)$_2$ (ref.[7]), benzylphenylhydroxylamine (BPHA), benzoylphenylhydroxylamine (BoPHA), benzylphenylnitrone (BPN), N-phenylbenzamide (N-PBA), dibenzylhydroxylamine (DBHA), dibenzylnitrone (DBN), diethylhydroxylamine (DEHA) (ref.[8]).
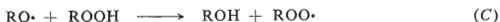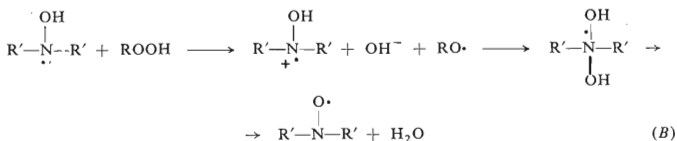
Procedures. The coordinated peroxy-radicals were prepared[19] by addition of TBHP (molar ratio 1 : 10) to 4 ml 0·05M benzenic solution of perfectly purified Co(acac)$_2$ under inert atmosphere at room temperature. The unreacted TBHP was distilled off in vacuum. The paramagnetic powdery residue was dissolved in benzene and anew evaporated in vacuum. In this way the system was rid of excess TBHP, and after dissolution in 4 ml benzene it exhibited an EPR signal with $g = 2·0147$ corresponding to 10^{-4}M peroxy-radicals. 0·2 ml solution of peroxy-radicals prepared was placed in EPR cell and treated with benzenic solution of the second reactant (concentration within 10^{-1} to 10^{-4} mol . l^{-1}). The spectra were measured and simulated with a Varian E—3 spectrometer and Varian SS—100 computer.

RESULTS AND DISCUSSION

The primary nitroxyl radicals. The mechanism of H abstraction of hydroxylamines by peroxy-radicals can be interpreted by the following scheme[16-18]

$$R_2'N—O—H + ROO \cdot \longrightarrow R_2'N—O \cdot + ROOH . \qquad (A)$$
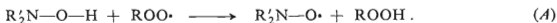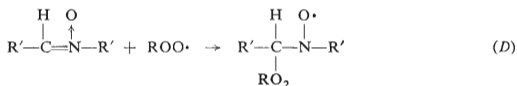
In the oxidation with hydroperoxides one elementary step must be presumed to involve an electron-transfer from the free electron pair at nitrogen to the hydroperoxide (as it was discussed in ref.[22]) according to the scheme:

$$R'—\overset{\overset{\displaystyle OH}{|}}{\underset{\cdot\cdot}{N}}—R' + ROOH \longrightarrow R'—\overset{\overset{\displaystyle OH}{|}}{\underset{+\cdot}{N}}—R' + OH^- + RO \cdot \longrightarrow R'—\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{N}}—R' \rightarrow$$

$$\rightarrow R'—\overset{\overset{\displaystyle O \cdot}{|}}{N}—R' + H_2O \qquad (B)$$

$$RO \cdot + ROOH \longrightarrow ROH + ROO \cdot \qquad (C)$$

We used the both types of the oxidation agents (ROO· and ROOH) in the oxidation of hydroxylamines, and we observed the primary nitroxyl radicals in accordance with the reactions (A) and (B). The splitting constants of their EPR spectra given in Table I agree well with the literature data[23,24].
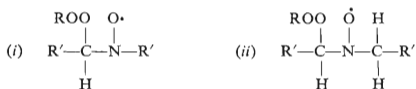
Further oxidation of the primary nitroxyl radicals with the peroxy-radicals is much faster than that with hydroperoxides. Whereas application of hydroperoxides results in stationary concentration of the primary nitroxyl radicals of about 10^{-3}M- in the case of peroxy-radicals the oxidation must be carried out at lower temperatures and/or lower concentrations of the peroxy-radicals to prevent formation of secondary products. Under the given conditions the concentration of the primary nitroxyl radicals is increased, if the methylene groups next to nitrogen (structures $IIIb$, IVb) are substituted by phenyl (structure Ib) or carbonyl group (structure IIb).

The secondary radicals. Reaction of the nitrones Ic, $IIIc$ with the coordinated peroxy-radicals gives the radical products Id, $IIId$ (Table I) according to the following scheme:

$$
\begin{array}{ccc}
\overset{\displaystyle H}{\underset{\displaystyle |}{}} \ \overset{\displaystyle O}{\underset{\displaystyle \uparrow}{}} & & \overset{\displaystyle H}{\underset{\displaystyle |}{}} \ \overset{\displaystyle O\cdot}{\underset{\displaystyle |}{}} \\
R'\!-\!C\!=\!N\!-\!R' + ROO\cdot & \rightarrow & R'\!-\!C\!-\!N\!-\!R' \\
& & \underset{\displaystyle RO_2}{|}
\end{array} \qquad (D)
$$

The obtained values of the splitting constants for Id, $IIId$ (Table I) agree well with the literature data[23,24] concerning similar structures. The radical products from the reactions of nitrones are identical with the secondary radical product from the reactions of the hydroxylamines, wherefrom it can be presumed that the gradual oxidation of hydroxylamines proceeds *via* the nitrones and leads to the same spin adduct. Influence of the reactant type, their molar ratios and temperature on the formation of the spin adducts is similar to that described for formation of the primary radicals. However, there is a marked difference in the secondary reactions depending on the oxidation reagent used (*i.e.* hydroperoxides or the coordinated peroxy-radicals).

Oxidation of the secondary radicals (spin adducts) by the coordinated peroxy- -radicals. The above-mentioned spin adducts can be described by the following structures:
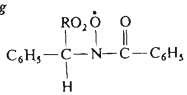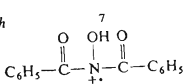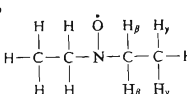
$$
\begin{array}{cc}
(i) \quad \begin{array}{c} ROO \ \ O\cdot \\ | \ \ \ \ | \\ R'\!-\!C\!-\!N\!-\!R' \\ | \\ H \end{array} & \qquad (ii) \quad \begin{array}{c} ROO \ \ \overset{.}{O} \ \ H \\ | \ \ \ \ | \ \ \ | \\ R'\!-\!C\!-\!N\!-\!C\!-\!R' \\ | \ \ \ \ \ \ \ \ | \\ H \ \ \ \ \ \ H \end{array}
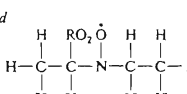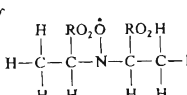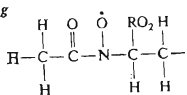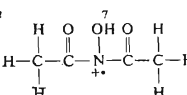\end{array}
$$

If hydroperoxides are used as the oxidation agents, then the concentration of the formed spin adducts (i) and (ii) remains practically unchanged. On the contrary, the coordinated peroxy-radicals oxidize these spin adducts and form another radicals. With increasing excess of the coordinated peroxy-radicals as compared with the

TABLE I

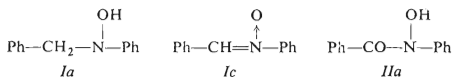The Observed Radical Structures and Assignment of Splitting Constants

Structure	Splitting constants, mT							
	a_N	$a_H^{\beta'}$	a_H^{β}	a_H^{γ}	$a_H^{2,6}$	$a_H^{3,5}$	a_H^4	a_H^7
Ib $C_6H_5-\overset{\overset{\displaystyle \dot{O}}{\vert}}{N}-\overset{\overset{\displaystyle H_\beta}{\vert}}{\underset{\underset{\displaystyle H_\beta}{\vert}}{C}}-C_6H_5$	1·055	—	0·570	—	0·275	0·095	0·275	—
Id $C_6H_5-\overset{\overset{\displaystyle \dot{O}}{\vert}}{N}-\overset{\overset{\displaystyle RO_2}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-C_6H_5$	1·070	—	0·175	—	0·265	0·087	0·265	—
IIb $C_6H_5-\overset{\overset{\displaystyle \dot{O}}{\vert}}{N}-\overset{\overset{\displaystyle O}{\parallel}}{C}-C_6H_5$	0·742	—	—	—	0·155	0·065	0·155	—
IIIb $C_6H_5-\overset{\overset{\displaystyle H_{\beta'}}{\vert}}{\underset{\underset{\displaystyle H_{\beta'}}{\vert}}{C}}-\overset{\overset{\displaystyle \dot{O}}{\vert}}{N}-\overset{\overset{\displaystyle H_\beta}{\vert}}{\underset{\underset{\displaystyle H_\beta}{\vert}}{C}}-C_6H_5$	1·515	0·877	0·877	—	—	—	—	—
IIId $C_6H_5-\overset{\overset{\displaystyle RO_2}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-\overset{\overset{\displaystyle \dot{O}}{\vert}}{N}-\overset{\overset{\displaystyle H}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-C_6H_5$	1·330	0·300	0·930 0·880	—	—	—	—	—
IIIf $C_6H_5-\overset{\overset{\displaystyle RO_2}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-\overset{\overset{\displaystyle \dot{O}}{\vert}}{N}-\overset{\overset{\displaystyle RO_2}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-C_6H_5$	1·150	0·122	0·122	—	—	—	—	—

TABLE I (Continued)

Structure	Splitting constants, mT							
	a_N	$a_H^{\beta'}$	a_H^β	a_H^γ	$a_H^{2,6}$	$a_H^{3,5}$	a_H^4	a_H^7
IIIg $C_6H_5-\overset{\text{RO}_2\overset{\cdot}{\text{O}}}{\underset{\text{H}}{C}}-N-\overset{O}{C}-C_6H_5$	0·700	0·100	—	—	—	—	—	—
IIIh $C_6H_5-\overset{O}{C}-\overset{7}{\underset{+\cdot}{N}}\overset{OH}{}-\overset{O}{C}-C_6H_5$	1·220	—	—	—	—	—	—	0·625
IVb $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{\cdot{O}}{N}-\overset{H_\beta}{\underset{H_\beta}{C}}-\overset{H_\gamma}{\underset{H_\gamma}{C}}-H_\gamma$	1·515	1·025	1·025	—	—	—	—	—
IVd $H-\overset{H}{\underset{H}{C}}-\overset{\text{RO}_2\overset{\cdot}{\text{O}}}{\underset{H}{C}}-N-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	1·355	0·338	1·090 0·940	—	—	—	—	—
IVf $H-\overset{H}{\underset{H}{C}}-\overset{\text{RO}_2\overset{\cdot}{\text{O}}}{\underset{H}{C}}-N-\overset{\text{RO}_2}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	1·150	0·155	0·155	—	—	—	—	—
IVg $H-\overset{H}{\underset{H}{C}}-\overset{O}{C}-\overset{\overset{\cdot}{O}}{N}-\overset{\text{RO}_2}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	0·706	—	0·050	0·025	—	—	—	—
IVh $H-\overset{H}{\underset{H}{C}}-\overset{O}{C}-\overset{7}{\underset{+\cdot}{N}}\overset{OH}{}-\overset{O}{C}-\overset{H}{\underset{H}{C}}-H$	1·225	—	—	0·018	—	—	—	0·532

substrate the reaction is faster adjusted in the region of higher oxidation degrees of the spin adducts, *i.e.* products of the type *f, g, h*.

The structure (i). With the aim of elucidation of oxidation of the spin adduct (i) we investigated reactions of the coordinated peroxy-radicals with the following reactants:
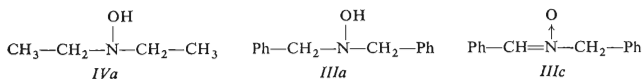
$$Ph-CH_2-\overset{\overset{\displaystyle OH}{|}}{N}-Ph \qquad Ph-CH=\overset{\overset{\displaystyle O}{\uparrow}}{N}-Ph \qquad Ph-CO-\overset{\overset{\displaystyle OH}{|}}{N}-Ph$$

Ia   *Ic*   *IIa*

It is a common feature of the reactants *Ia, Ic* and *IIa* that their oxidation gives the same final product (benzoylphenylnitroxyl radical) whose experimental and simulated spectra are given in Fig. 1. However, in the oxidation of *Ia* it is possible to observe the intermediates *Ib* and *Id*, and in that of *Ic* the intermediate *Id* is observed, too. This fact can be reasonably explained by the Scheme 1 from which it follows that
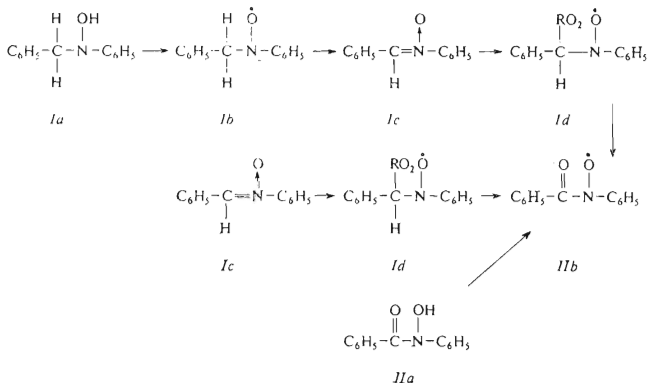
SCHEME 1

methylene or methine groups next to nitroxy group can be oxidized with the co-ordinated peroxy-radicals as far as to carbonyl group.

The structure (ii). Further we oxidized the following substrates containing two methylene or methine groups next to nitrogen:

$$CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{N}-CH_2-CH_3 \qquad Ph-CH_2-\overset{\overset{\displaystyle OH}{|}}{N}-CH_2-Ph \qquad Ph-CH=\overset{\overset{\displaystyle O}{\uparrow}}{N}-CH_2-Ph$$

IVa   *IIIa*   *IIIc*

In analogy to the above case, the spin adducts *IIId* and *IVd* derived from the substrates *IIIa* and *IVa* or *IIIc* form new types of radicals *IIIf,g,h* and *IVf,g,h* whose
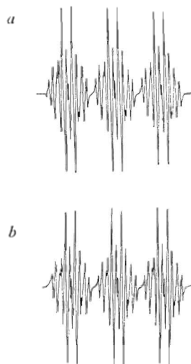

a

b

FIG. 1

The Experimental and Simulated Spectra Obtained in Reaction of Benzylphenyl-hydroxylamine with Coordinated Peroxy--Radicals
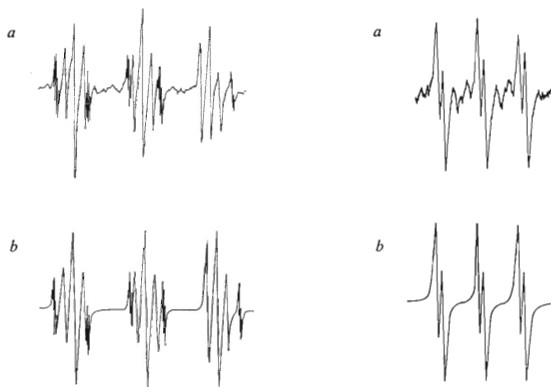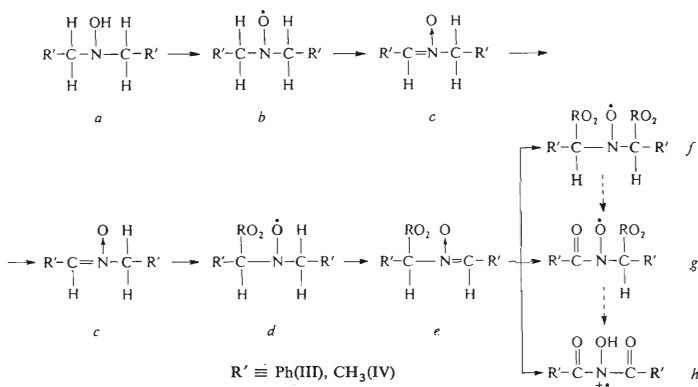
a Experimental, *b* simulated.

FIG. 2

The Experimental and Simulated Spectra Obtained in Reaction of Dibenzylhydroxylamine with Coordinated Peroxy-Radicals (*a, b* see Fig. 1)

experimental and simulated spectra are given in Figs 2 and 3. Their formation can be described by Scheme 2.
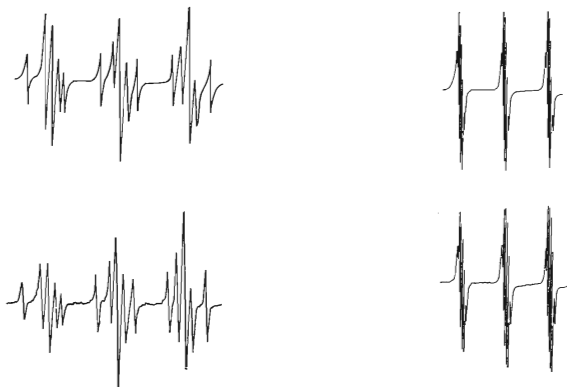

SCHEME 2

Fig. 3

The Experimental and Simulated Spectra Obtained in Reaction of Diethylhydroxylamine with Coordinated Peroxy-Radicals

The results of reactions of structures (i) indicated that the respective products can be gradually oxidized by the coordinated peroxy-radicals in a cycle spin adduct — nitrone — spin adduct. It was shown that final result of such oxidation of methylene or methine group is their conversion to carbonyl group. Similarly to the case of the structure (i), for (ii) we also presume that the radicals $IIId, IVd$ are formed from the spin adducts $IIIf, IVf$, respectively. Oxidation of their methine groups to carbonyl groups results in formation of $IIIg, IVg$ and $III\,h, IVh$, respectively. Values of the found splitting constants correlate with the presumed structure. For similar spin adducts the found splitting constants of methine proton and nitrogen are about 0·15 and 1·3 mT, respectively[24]. For the product $IIIf$ we have found $a_H = 0.122$ mT, $a_N = 1.15$ mT; for IVf $a_H = 0.155$ mT, $a_N = 1.15$ mT. In this context it is worth mentioning that gradual substitution of hydrogen atoms of methylene or methine groups by oxygen groups (structures $IIId,f,g$ and IVd,f,g) results in lowering of spin density of the unpaired electron at the nitrogen nucleus as it follows from the decrease in the splitting constants a_N given in Table I. In the series of these oxidation products it is, however, remarkable that the a_N values again markedly increase for the structures $IIIh$ and IVh. This fact indicates their special standing, and it can be connected with their probably being in the form of ion-radicals in contrast to $IIId,f,g$ and IVd,f,g which represent neutral nitroxyl radicals. Experimental and simulated spectra of the mentioned structure "h" are given in Figs 2 and 3. Formulation of these structures and assignment of the splitting constants (Table I) are supported by the following consideration. The hyperfine splitting $a_H = 0.018$ mT found for

IVh was observed in a similar case of radical (IVg) for the grouping $—\overset{\overset{\displaystyle O\cdot}{|}}{N}—COCH_3$. Two equivalent methylene groups with the centre of the unpaired electron at nitrogen

correspond (in the spectrum) to the partial structure $— \overset{\overset{\displaystyle O\cdot}{|}}{N}—(COCH_3)_2$. The proton with $a_H = 0.532$ and 0·625 mT (for IVh and $IIIh$, respectively) can thus be localized in the centre of the radical on the following two structures h and h':

$$R' = CH_3, Ph$$

$$(III, IV)h \qquad (III, IV)h'$$
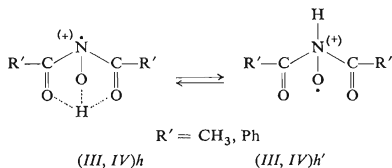
We suppose the structures "h" to be more probable than "h'", because the former show more extended stabilization of the proton by the neighbouring carbonyl groups.

Another alternative explaining the obtained data for products *IIIh* and *IVh* is according to our latest investigations the formation of airidinyl-1-oxyl radicals.

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