HYDROGEN AND ELECTRON TRANSFER FROM DIPHENYLAMINE IN REACTION WITH COORDINATED PEROXY-RADICALS AND HYDROPEROXIDES*

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Reaction of diphenylamine with coordinated peroxy-radicals and various hydroperoxides (tert-butyl hydroperoxide, cumene hydroperoxide, tetraline hydroperoxide) has been studied in non-polar solvents by the EPR method. From this kinetic study the activation energies of H-transfer (105 ± 2 kJ/mol in the temperature range —40 to —10°C) and e-transfer (97 ± 2 kJ/mol in the temperature range 10 to 50°C) have been determined. From the activation energies it follows that, in a reaction mixture containing simultaneously a hydroperoxide and initiating peroxy-radicals, oxidation of diphenylamine goes by the both parallel mechanisms until the final concentration of nitroxyl radical reaches the value of about $1\cdot7 \cdot 10^{21}$ spin/l.

According to Boozer and Hammond[1] recombination of nitroxyl radicals with initiating peroxy-radicals makes the most substantial contribution to oxidation inhibition of hydrocarbons in the presence of diphenylamine (DPA). Later Thomas and Tolman[2] presumed formation of the activated complex between alkylperoxy-radicals and DPA to be the most significant factor in the course of the H-transfer, which results in inactivation of the primary oxygen radicals. Generally amines with suitable steric properties acting as antioxidants are not only donors of hydrogen atom, but also decompose hydroperoxides at laboratory temperature[3], which is made use of for initiation of polymerization or cross linking of polymers.

The aim of this work is a study of the both mentioned types of transfer processes, *viz.* of hydrogen atom or electron from the free electron pair at nitrogen, using the EPR method in the reaction of DPA with the coordinated, continually produced free peroxy-radicals[4] or with hydroperoxides: tert-butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP), tetraline hydroperoxide (THP). This combined approach enabled investigation of the individual components of the highly efficient oxidation system[4,5,23] containing up to 10^{-4}M of the initiating coordinated tert-butyl peroxy-radicals formed by reaction of cobalt acetylacetonate ($Co(acac)_2$) with excess TBPH in non-polar solvents at room temperature. This study can explain the experimental fact that the system Co(II)–hydroperoxide generates a substantially

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higher concentration of the secondary nitroxyl radicals from DPA than the oxidation systems in which the primary ROO· radicals are generated by thermal decomposition of peroxides or photochemically.

EXPERIMENTAL

Method A. Reaction of 0·05M $Co(acac)_2$ with excess TBHP (molar ratio 1 : 10) in perfectly dried non-polar solvents (benzene, hexane, CCl_4) leads to stationary concentration of the coordinated radicals and, besides that, to continually produced free ROO· radicals[5] which give molecular oxygen on recombination. In the reactions of $Co(acac)_2$ with CHP or THP the molar ratio was 1 : 1. This system exhibited EPR signal of the coordinated peroxy-radicals ($g = 2{\cdot}0147$) for all types of the hydroperoxides used, and sublimed DPA was added thereto in various concentrations in the same volume amount within concentration range $2{\cdot}5 \,.\, 10^{-1}$ to $5 \,.\, 10^{-3}$ mol . l^{-1} either in a closed reaction vessel under inert atmosphere with stirring (magnetic stirrer) or direct in the EPR cell. In the reaction of $Co(acac)_2$ with TBHP at room temperature an about 10^{-4} mol . . l^{-1} concentration of the peroxy-radicals is formed 5 min after mixing the reaction components whereas analogous reactions with CHP or THP produce about 10^{-5}mol . l^{-1} concentrations. If DPA is dissolved direct in 0·05M $Co(acac)_2$ solution and the respective hydroperoxide is added, then the primary coordinated peroxy-radicals are not observed; instead the EPR signal of nitroxyl radicals (characterized by the basic triplet splitting) appears and increases with time. Time dependence of this signal intensity at various temperatures provided kinetic parameters for study of the radical reaction of DPA.

Method B. This procedure of preparation of the primary coordinated peroxy-radicals differs from the "method A" in that the H-transfer between DPA and the coordinated ROO· radicals takes place without the excess of hydroperoxide and, hence, without formation of free peroxy-radicals and molecular oxygen[6]. The excess unreacted hydroperoxide from the reaction according to the method A is removed by evaporation in vacuum at 10 to 15°C. The obtained residue is dissolved in benzene and the evaporation is repeated. The final dissolution gives a practically unchanged original concentration of the coordinated peroxy-radicals.

Method C. For preparation of the coordinated alkoxy-radicals we used the described method[7] *i.e.* reaction of ditert-butyl peroxalate with $Co(acac)_2$ at room temperature.

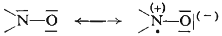
Apparatus. We used an EPR spectrometer Varian E-3 in the range X with 100 kHz modulation combined with Variable temperature accessory Varian enabling to maintain the sample temperature in the resonance cavity within ±1°C. The spectra were simulated with a SS-100 apparatus.

Reagents. Tert-butyl hydroperoxide (TBHP) 93% (Fluka, Switzerland); cumene hydroperoxide (CHP) 92% obtained by vacuum concentration of commercial product (Lachema, Brno); tetraline hydroperoxide (THP) 94% was prepared by oxidation of tetraline ditert-butylperoxalate, (DBPO) was prepared from tert-butyl hydroperoxide and oxalyl chloride in the presence of pyridine[24]. Diphenylamine (DPA) was purified by crystallization from ethanol under inert atmosphere in dark and by subsequent sublimation in vacuum (133·32 Pa). Cobalt acetylacetonate ($Co(acac)_2$) was prepared by the procedure described by Charles and Pawlikowski[22]. It was dried before use in vacuum (1 333·2 Pa) at 120°C.

RESULTS AND DISCUSSION

H-*Transfer*. Homolytic splitting of NH bond in DPA has been studied so far by various oxidation systems giving nitrogen or nitroxyl radicals[8–13]. The elementary process of hydrogen abstraction by oxygen radicals produces reactive nitrogen radicals with short life-time the low level of which can be indicated by continuous flow technique only during irradiation of the sample with UV or ionisation radiation in inert medium[8-10]. On the contrary, nitroxyl radicals exhibit considerable stability in non-polar solvents[11-13], and their accumulation and kinetics of formation can be followed directly by EPR method.

As the unpaired electron of the radical generated from DPA is predominantly concentrated at nitrogen, the splitting constant is $a_N = 0{\cdot}880$ mT, on the contrary, if the unpaired electron is localized predominantly at oxygen of nitroxyl radical and is stabilized by resonance, then the value of splitting constant depends on the solvent polarity, being $a_{NO} = 0{\cdot}930$ and $1{\cdot}140$ mT in non-polar and polar solvents, respectively.



$$>\dot{N}-\overline{\underline{O}} \longleftrightarrow >\overset{(+)}{\underset{\cdot}{N}}-\overline{\underline{O}}|^{(-)} \qquad (A)$$

For the nitroxyl radicals the spin density at carbon atoms is the same with *ortho* and *para* hydrogen atoms $a_H^{o,p} = 0{\cdot}183$ mT (septet), being different for *meta* hydrogen $a_H^m = 0{\cdot}079$ mT (quintet). For the nitrogen radical the values of the corresponding splitting constants are considerably higher (four *ortho* protons, $a_H^o = 0{\cdot}368$ mT, two *para* protons, $a_H^p = 0{\cdot}428$ mT, and four *meta* protons, $a_H^m = 0{\cdot}152$ mT). Spin density transfer from nitrogen atom to benzene ring enables to differentiate the EPR signals of nitrogen radicals from those of nitroxyl radicals.

Nitroxyl radicals are formed by a secondary attack of the primary nitrogen radical by peroxy-radicals[14,15]

$$>NH + ROO\cdot \rightarrow >N\cdot + ROOH \qquad (B)$$

$$>N\cdot + ROO\cdot \rightarrow >N-O\cdot + RO\cdot . \qquad (C)$$

In the absence of ROO· radicals, a direct attack by RO· radicals is a prerequisite of generation of nitrogen radicals. The EPR signal obtained in the reaction of ditert-butyl peroxalate (DBPO) with $Co(acac)_2$ (method (*C*)) is identical with that obtained in the reaction of TBHP with $Co(acac)_2$ in the presence of DPA (method B) where the coordinated peroxy-radicals are formed (Fig. 1). From spectral simulation (splitting constants $a_{NO} = 0{\cdot}940$ mT, $a_H^o = a_H^p = 0{\cdot}181$ mT, $a_H^m = 0{\cdot}081$ mT) it follows that signals of nitroxyl radical are only observed in the final phase irrespective of the method of generation ((*B*) the same as (*C*)). The only difference is in a small increase of g-factor corresponding to a decrease of the resonance magnetic field by 0·1 mT. After a short time the value of the g-factor is fixed at $g = 2{\cdot}0073$ corresponding to the nitroxyl radicals. Oxidation of DPA (as we shall show later) also produces hydroxylamine which can be a source of nitroxyl radicals, and with excess DBPO it is also impossible to exclude an induced decomposition of DBPO to ROO· radicals in the presence of DPA. Thus in the further kinetic study the EPR signals with basic triplet splitting correspond to nitroxyl radicals.

H-*Transfer kinetics*. The activation energy of hydrogen-transfer from DPA to the coordinated ROO· radicals in the absence of hydroperoxide (method (*B*)) was determined by means of kinetic curves of generation of nitroxyl radicals within the temperature range −40 to −15°C (Fig. 2). At higher temperatures the reaction was so fast that it was impossible to record the concentration changes of nitroxyl radicals with time by the usual EPR technique. Autocatalytic character is marked especially in the low-temperature range. After crossing the induction period the level of nitroxyl radicals increases initially exponentially. The linear section of the curves after reaching the maximum velocity was used for determination of the maximum velocity v_{max} of the H-transfer. The Arrhenius dependence of log v_{max} *vs* $1/T$ (Fig. 3) is linear, and its slope was used for determination of the activation energy value of hydrogen transfer from amino group of DPA to the coordinated peroxy-radicals (105 ± ± 2 kJ/mol). The found value is about 2× greater than that found for the H-transfer from OH group of unhindered phenols to the coordinated peroxy-radicals[16]. In spite of that, the reached final concentration of the secondary generated nitroxyl radicals is substantially higher than that of phenoxy-radicals under the same reaction conditions. This fact explains the autocatalytic course of the kinetic curves with typical S shape. If phenols or bisphenols are the source of hydrogen for H-transfer[17–19],

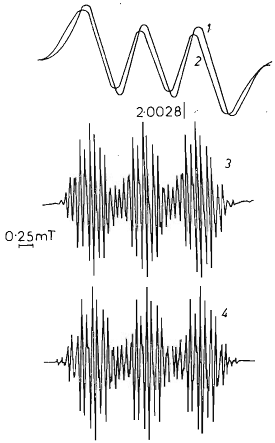


FIG. 1

EPR Signals of the Nitroxyl Radicals Generated from DPA in Benzene Solution by Peroxy-Radicals *1*, *3* and Alkoxy-Radicals 2, *4* at Room Temperature then the level of secondary phenoxy-radicals is fixed practically immediately at room temperature without any subsequent kinetics.

e-*Transfer*. The primary complexes between amines and peroxides are decomposed at room temperature in a reaction cage with partially ionic heterolytic splitting of O—O bond or by radical way with partial homolytic decomposition[15,18]. The ionic and homolytic decompositions are preferred in polar and non-polar solvents, respectively. A prerequisite of homolytic decomposition of hydroperoxide is the transfer of one electron from free electron pair at nitrogen with transient formation of cation-radical. Similarly, unstable cation-radicals are formed by electron-transfer from sulphur atom of thiobisphenols to hydroperoxides[19,20] or from phosphites to hydroperoxides[21]

$$>S: + ROOH \rightarrow >\overset{+}{S}\cdot + OH^- + RO\cdot \rightarrow >\dot{S}—OH \qquad (D)$$

$$>P: + ROOH \rightarrow >\overset{+}{P}\cdot + OH^- + RO\cdot \rightarrow >\dot{P}—OH \qquad (E)$$

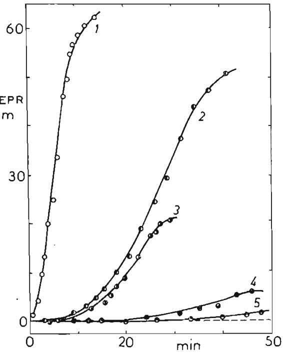


FIG. 2

Dependence of I_{EPR} of Signal of Nitroxy within Temperature Interval —15 to —40°C Generated by the Method B *1* —15°C, *2* —20°C, *3* —25°C, *4* —30°C, *5* —40°C

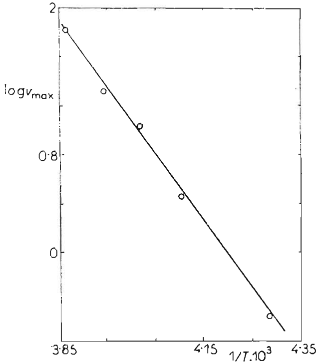


FIG. 3

Dependence of lg v_{max} of Formation of Nitroxyl Radicals on $1/T$ (calculated from the curves in Fig. 2)

If the free electron pair is removed *e.g.* by oxidation of the sulphides to sulphones or phosphites to phosphates, then the free radicals are not formed in the presence of hydroperoxides.

e-*Transfer kinetics.* Kinetics curves of formation of nitroxyl radicals with time have linear course (Fig. 4) for various initial molar ratios DPA : TBHP. Using the same temperature and benezne solutions, we observed the highest final concentration of the generated nitroxyl radicals at the molar ratio DPA : TBHP = 1 : 4. Obviously the excess of TBHP determined the equilibrium concentration of the primary complex between DPA and TBHP dimer in which the e-transfer takes place connected with radical decomposition of peroxidic bond. From kinetic study within the temperature interval 15–50°C we determined the activation energy of the electron transfer 97 ± 2 kJ/mol (Fig. 5). As this value is lower than the activation energy of the H-transfer by about 8 kJ/mol, it can be presumed that in the oxida-

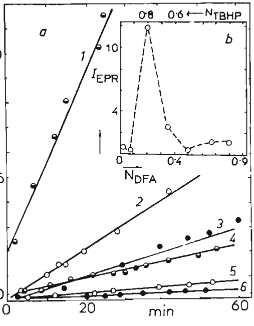


FIG. 4

Time Dependence of I_{EPR} of Signal of Nitroxyl Radicals (23°C) in Reaction of DPA with TBHP at Various Molar Ratios TBHP : : DPA (*a*); Dependence of I_{EPR} of the Signal on Molar Ratio TBHP : DPA after 30 min Reaction (*b*)

TBHP : DPA *1* 4 : 1, *2* 2 : 1, *3* 1 : 4, *4* 1 : 2, *5* 10 : 1, *6* 1 : 1.

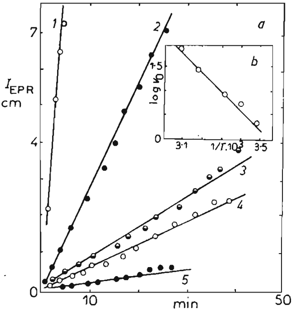


FIG. 5

Time Dependence of I_{EPR} of Signal of Nitroxyl Radicals in Reaction of DPA with TBHP (molar ratio 1 : 4) at Various Temperatures (*a*)

1 50°C, *2* 40°C, *3* 30°C, *4* 20°C, *5* 15°C. (*b*) Dependence of lg v_0 (formation rate of nitroxyl radicals) on $1/T$.

tion with the coordinated peroxy-radicals in the presence of the unreacted hydroperoxide the e-transfer will take place along with the hydrogen transfer.

Quantitative analysis of level of the coordinated and the continuously generated peroxy-radicals tested by DPA. In recent studies of hydrogen transfer from various H-donors (—OH, —SH, —NH) the system $Co(acac)_2$–hydroperoxide (method (*A*)) in non-polar solvents is applied as an efficient system for generation of unusually high concentration of secondary free radicals as the H-transfer products. If the respective antioxidant as a H-donor is allowed to react with the initiating peroxy-radicals under these dynamic conditions of excess hydroperoxide, it is possible to generate substantially higher level of secondary nitroxyl radicals than that in the oxidation by only the coordinated peroxy-radicals with exclusion of the unreacted excess of hydroperoxide according to the method B. This fact was explained by simultaneous continuous formation of free tert-butylperoxy-radicals (TBHP) in the presen-

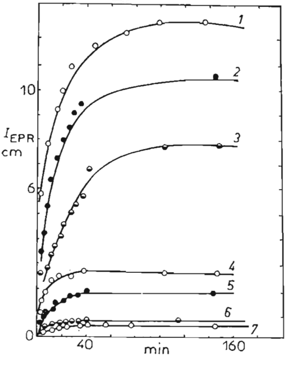


FIG. 6

Time Dependence of I_{EPR} of Signal of Nitroxyl Radicals (23°C) in Oxidation of DPA by Method A at Various Molar Ratios TBHP : Co

1 10 : 1, *2* 7 : 1, *3* 5 : 1, *4* 2 : 1, *5* 1 : 1, *6* 1 : 2, *7* 1 : 4. DPA concentration $5 \cdot 10^{-2}$ mol/dm^3, benzene as solvent.

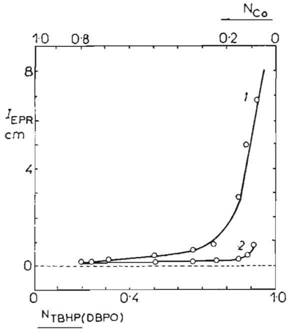


FIG. 7

Dependence of I_{EPR} of Signal on Molar Ratio TBHP : Co *1* and DBPO : Co *2* at Room Temperature in Benzene ce of excess hydroperoxide along with the coordinated radicals[4]. DPA is a suitable H-donor for quantitative testing of individual contributions of the reacting components of the oxidation system. Whereas the level of the coordinated radicals is fixed at a value 10^{-4} mol . l^{-1} after mixing the reactants (*i.e.* it can be indicated by the EPR technique), the same is not true of the continuously generated ROO· radicals whose stationary concentration is lower by about two orders of magnitude. Low activation energy of recombination of free ROO· as compared to that of the coordinated ROO·[16] causes their short life time so that the corresponding EPR signals can be indicated only by rapid "flow" technique.

Kinetics of generation of the secondary nitroxyl radicals from DPA at various initial concentrations of the coordinated peroxy-radicals according to the method (*A*) is given in Fig. 6. From the moment the reaction is started the concentration of nitroxyl radicals increases at maximum velocity at room temperature, and this rate gradually decreases, until it reaches zero value in the stationary region. The final level of nitroxyl radicals in the stationary region is the higher the higher was the original concentration of peroxy-radicals. Starting from the molar ratio Co : TBHP = 1 : 1, the concentration of the initiating coordinated peroxy-radicals increases with increasing concentration of TBHP and reaches its maximum at the molar ratio Co : TBHP = 1 : 10 (Fig. 7). Thus it is possible to investigate the quantitative relations between the amount of the generated secondary nitroxyl radicals and concentration of the initiating coordinated peroxy-radicals (Fig. 8). From the simplified diagram it can be seen that, though concentration of the coordinated peroxy-radicals in the oxidation system is low (below 10^{14} spin/0·1 ml) up to the ratio Co : TBHP = 1 : 1, it is possible to generate $5 . 10^{15}$ to 10^{16} spin/0·1 ml nitroxyl radicals by e-transfer from DPA to hydroperoxide. At the molar ratios Co : TBHP above 1 : 1 there are generated $10^{16}-10^{17}$ spin/0·1 ml of nitroxyl radicals in benzene solution with simultaneous initiation concentration of peroxy-radicals $5 . 10^{15}$ spin/0·1 ml. Such increase in amount of nitroxyl radicals can be explained by continuous generation of free ROO· radicals produced in the presence of excess TBHP in the system. Another source of the coordinated ROO· radicals can also be in coordinated tetroxides[4].

If stabilized alkoxy-radicals are used for initiation of the nitroxyl radicals (absolute concentration of the former is lower than that of the coordinated peroxy-radicals by about one order of magnitude), then the amount of the nitroxyl radicals reaches about $9 . 10^{15}$ per 0·1 ml of benzene solution at the molar ratio Co : DBPO = 1 : 10 (Fig. 9).

Testing of capacity of radical initiation systems for H- or e-transfer based on $Co(acac)_2$/hydroperoxide in the presence of DPA characterized quantitatively the contribution of individual initiation systems leading to accumulation of the nitroxyl radicals. This fact is expressed in a summarized diagram (Fig. 10). From the time dependence of logarithm of concentration of the nitroxyl radicals generated at the same temperature in the same time it follows that the highest level of nitroxyl radicals is reached in the initiation system with excess hydroperoxide where their generation proceeds dynamically (method (*A*)), curve *1*. After 30 min the amount of nitroxyl radicals equals $1 . 10^{17}$ spin/0·1 ml. If the radicals are generated from DPA by only electron transfer, *i.e.* in the presence of TBHP without $Co(acac)_2$, the final level of radicals is ten times lower after the same time, *viz.* $3 . 10^{16}$ spin/0·1 ml – curve 2. If the nitroxyl radicals are initiated by only the coordinated peroxy-radicals – method B, *i.e.* in the absence of any excess unreacted hydroperoxide, the nitroxyl radicals level reaches $5 . 10^{15}$ spin/0·1 ml which is approximately equivalent to concentration of the initiating coordinated peroxy-radicals. If the nitroxyl radicals are generated by cobalt(III) dihydroxytetrakisacetylacetonate $(Co(III)L_2OH)_2$ their concentration is lower by one order of magnitude in the stationary region, *i.e.* $3 . 10^{14}$ spin/0·1 ml – curve *4*. The cobalt(III) acetylacetonate itself does not react with DPA in benzene solution and gives no nitroxyl radicals. If we try to explain the fact that concentrations of the nitroxyl radicals generated by the dynamic method (*A*)

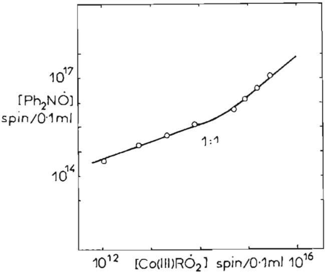


FIG. 8

Dependence of Amount of Nitroxyl Radicals on Concentration of the Coordinated RO_2 Radicals in Benzene at Room Temperature (method (*A*))

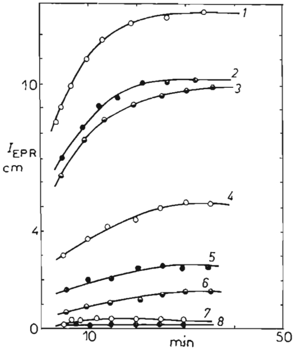


FIG. 9

Time Dependence of I_{EPR} of Signal of Nitroxyl Radicals (23°C) in Reaction of DPA with Oxidation System Containing RO Radicals (method (*C*)) at Various Molar Ratios DBPO : Co

1 10 : 1, *2* 7 : 1, *3* 5 : 1, *4* 3 : 1, *5* 2 : 1, *6* 1 : 1, *7* 1 : 2, *8* 1 : 4. DPA concentration $5 . 10^{-2}$ mol dm^3, benzene as solvent.

are substantially higher than the level of the coordinated peroxy-radicals indicated by the EPR method, two alternatives can be considered: (i) an autocatalyzed chain mechanism of generation of nitroxyl radicals (with exponential course) and (ii) continuous generation of free peroxy-radicals in the catalytic circle

$$\mathrm{Co(acac)_2OH + ROOH \rightarrow Co(acac)_2 + ROO\bullet + H_2O} \qquad (F)$$

$$\mathrm{Co(acac)_2 + ROOH \rightarrow Co(acac)_2OH + RO\bullet} \qquad (G)$$

$$\mathrm{RO\bullet + ROOH \rightarrow ROH + ROO\bullet}\,. \qquad (H)$$

Systematic studies of H-transfer between the coordinated peroxy-radicals and phenols or bisphenols[19] showed that the final level of phenoxy-radicals generated by the H-transfer initiated by the coordinated peroxy-radicals is lower than that of the original initiation radicals, and the H-transfer is established immediately after mixing the reactants at room temperature. On the contrary, in the radical attack of DPA we can see a substantially different kinetic course of generation of nitroxyl radicals. At the beginning their concentration increases exponentially and (as we have already told) reached substantially higher values in the stationary region of the kinetic curves as compared with the secondary phenoxy-radicals. Generation of the phenoxy-radicals by the coordinated peroxy-radicals is conditioned

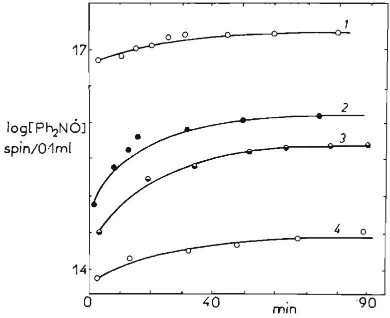


FIG. 10

Time Dependence of lg of Nitroxyl Radixal Concentration in Oxidation of DPA with Various Initiation Systems

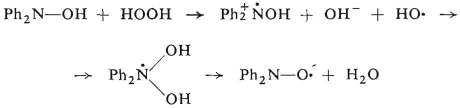
1 Method A, *2* TBHP, *3* method B, *4* $(CoL_2OH)_2$ at room temperature.

by formation of primary associate between cobalt and the original phenol. In contrast to phenols, DPA (which does not form complexes with cobalt, but forms complexes with hydroperoxide dimer) does not block the catalytic circle of the electron transfer from cobalt to hydroperoxide and, hence, the continuous generation of the initiating free peroxy-radicals until complete exhaustion of the hydroperoxide.

In the complex between DPA and hydroperoxide the electron transfer can take place from the free electron pair at nitrogen of DPA to the peroxidic bond, the products in the reaction cage being hydroxylamine and alcohol:

$$Ph_2NH + ROOH \rightarrow Ph_2^+\dot{N}H + RO\cdot + OH^- \rightarrow Ph_2NOH + ROH. \qquad (I)$$

The presumed intermediate diphenyl hydroxylamine decomposes hydroperoxide by analogous electron transfer from free electron pair of nitrogen, the final products being nitroxyl radicals and water; a similar course was found by Albuin and coworkers[17] in the reaction of dimethylhydroxylamine with H_2O_2.



$$Ph_2N{-}OH + HOOH \rightarrow Ph_2^+\dot{N}OH + OH^- + HO\cdot \rightarrow$$

$$\rightarrow Ph_2\dot{N}\begin{array}{l}{}^{\diagup}OH\\ {}_{\diagdown}OH\end{array} \rightarrow Ph_2N{-}O\cdot + H_2O \qquad (K)$$

The intermediate alkoxy- or peroxy-radicals attack DPA directly to give a nitrogen radical and finally the stable nitroxyl radical.

To sum up, reaction of hydroxylamines with hydroperoxides produces two intermediate free radicals, which explains exponential course of generation of nitroxyl radicals in oxidation of DPA by the dynamic method A. If it is taken into account that the original reaction mixture (before oxidation) contained $3 . 10^{19}$ DPA molecules per 0·1 ml, and $1{\cdot}77 . 10^{18}$ nitroxyl radicals per 0·1 ml was detected by the EPR method after the oxidation, it is obvious that 5·6% DPA reacted by H- and e-transfers to give stable nitroxyl radicals. This fact excludes the presumption that the nitroxyl radicals take part in inactivation of oxygen radicals by recombination at room temperature or lower temperatures, which was presumed by Boozer and Hammond[1]. Quantitative analysis indicates that predominant part of these nitroxyl radicals (about 90%) is formed by catalytic generation – e-transfer from cobalt to hydroperoxide, whereas 10% is formed by direct H-transfer to the coordinated ROO• radicals and e-transfer from the free electron pair at nitrogen to hydroperoxide. In a further study the process is analyzed of generation of nitroxyl radicals in the presence of hydroxylamines. When the absorbance change of =NH group is followed quantitatively by IR spectroscopy in the course of oxidation of DPA by the method (*A*), its quantitative decrease is found to be at a value similar to the level of the generated nitroxyl radicals indicated by the EPR method.

REFERENCES

1. Boozer C. E., Hammond G. S.: J. Amer. Chem. Soc. *76*, 3861 (1954).
2. Thomas J. R., Tolman C. A.: J. Amer. Chem. Soc. *84*, 2930 (1962).
3. Mikulášová D., Horie K., Tkáč A.: Eur. Polym. J. *10*, 1039 (1974).
4. Tkáč A., Veselý K., Omelka L., Přikryl R.: This Journal *40*, 117 (1975).
5. Přikryl R., Tkáč A., Malík Ľ., Omelka L.: This Journal *40*, 103 (1975).
6. Tkáč A. J. Polym. Sci. Symp. *57*, 121 (1976).
7. Tkáč A., Veselý K., Omelka L.: This Journal *39*, 3504 (1974).
8. Neugebauer F. A., Bamberger S.: Chem. Ber. *107*, 1788 (1974).
9. Shanshal M.: Z. Naturforsch. *28a*, 1892 (1973).
10. Shimonov G. S.: Zh. Fiz. Khim. *46*, 2324 (1972).
11. Fischer P. H. H., Neugebauer F. A.: Z. Naturforsch. *19a*, 1514 (1964).
12. Aurich H. G., Baer F.: Tetrahedron Lett. *1965*, 3879.
13. Ayscough P. B., Sealy R. C., Woods D. E.: J. Phys. Chem. *75*, 3454 (1971).
14. Buchachenko A. L.: *Stabilnye Radikali.* Khimiya, Moscow 1973.
15. Swern D.: *Organic Peroxides*, Vols I, II, III. Wiley, London 1972.
16. Tkáč A., Omelka L.: Org. Magn. Resonance, *14*, 109 (1980).
17. Albuin E., Encina M. V., Diaz S., Lissi A. A.: Int. J. Chem. Kinet. *10*, 677 (1978).
18. Buchachenko A. L.: *Chemická polarizácia elektrónov a jadier* (translated from Russian). Veda, Bratislava 1979.
19. Tkáč A., Omelka L., Jiráčková L., Pospíšil J.: Org. Magn. Resonance *14*, 171 (1980).
20. Tkáč A., Omelka L., Jiráčková L., Pospíšil J.: Org. Magn. Resonance *14*, 249 (1980).
21. Tkáč A., Ruger C., Schwetlick K.: This Journal *45*, 1182 (1980).
22. Charles R. G., Pawlikowski M. A.: J. Phys. Chem. *62*, 440 (1958).
23. Tkáč A., Veselý K., Omelka L.: J. Phys. Chem. *75*, 2575 (1971).
24. Bartlett P. D., Benzing E. P., Pincock R. E.: J. Amer. Chem. Soc. *82*, 1762 (1960).

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