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Nitroxy-radicals in the Liquid-phase Oxidation Reactions of Organic Compounds

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The review is devoted to the mechanism of the action of stable nitroxy-radicals in liquid-phase oxidation reactions of organic compounds. The chemical reactions which take place with participation of nitroxy-radicals are examined and their kinetic parameters are presented. The causes of the high inhibition coefficients and the possible ways of regenerating the nitroxy-radicals from their reaction products are discussed. The phenomenon of the selective inhibition of polymerisation processes accompanying oxidation is described and the conditions necessary for selective inhibition and the possibility of using nitroxy-radicals for this purpose are discussed.
The bibliography includes 97 references.

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I. INTRODUCTION

Stable nitroxy-groups are nowadays finding increasing application in various branches of scientific research and in industrial practice. In particular, they are used as stabilisers in the storage of organic substances, as spin labels and paramagnetic probes in molecular biophysics, and as acceptors and counters of free radicals in the study of the mechanisms of chemical reactions. Numerous data concerning the ways of preparation, properties, and applications of nitroxy-radicals have been published.[1-7] The principal characteristic of nitroxy-radicals, which distinguishes them from other stable organic radicals, is the absence of delocalisation of the unpaired electron.[1,8]

One of the causes of the great interest shown in nitroxy-radicals is that they are effective stabilisers of the oxidative degradation and photodegradation of polymers, in the first place polyolefins.[9-20] The characteristic features of the action of nitroxy-radicals as UV-stabilisers of polymeric materials have been examined in detail,[11,14] but much less attention has been devoted to problems of their antioxidant stabilisation. It is known that many processes occurring in polymers can be successfully investigated using simpler reactions with participation of low-molecular-weight substances, for example, monomers, as models. The study of the mechanism of the action of nitroxy-radicals in the oxidation of monomers is of interest also from this point of view. The criteria of the applicability of such monomeric models to the solution of problems in the field of the degradation and stabilisation of polymers have been formulated.[9,21-23]

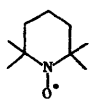
This review is devoted to the action of nitroxy-radicals in the liquid-phase oxidation reactions of monomeric organic compounds which make it possible to obtain many important products of organic synthesis. Fairly numerous interesting results exist in this field but hitherto they have not been surveyed or described systematically. The review deals with the principal experimental data obtained in the study of the reactions of nitroxy-radicals in chain oxidation processes during the last 20–25 years, i.e. virtually since the inception of this field of research. This led to a number of generalisations and certain mathematical relations describing the action of nitroxy-radicals in oxidation systems are given.

II. CHEMICAL REACTIONS WITH PARTICIPATION OF NITROXY-RADICALS IN OXIDATION REACTIONS OF ORGANIC COMPOUNDS

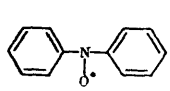
Stable nitroxy-radicals are able to inhibit radical chain processes. The inhibiting effect of nitroxy-radicals is due to the fact that they are able to enter into reactions, involving the saturation of the valence, with other species having an unpaired electron, in particular with free organic radicals propagating the oxidation chain.

For an oxidative chain reaction, it is possible to determine even from concentration relations which of the radicals, the alkyl radical $R^{\cdot}$ or the peroxy-radical $RO_2^{\cdot}$, participates in chain termination (i.e. in recombination by adding to the nitroxy-radical). If the chain of oxidation depends on the partial pressure of O_2 in the system, this means that the radicals $R^{\cdot}$ are responsible for the chain termination. When the rate of reaction is independent of the oxygen content, the $RO_2^{\cdot}$ radicals are responsible for chain termination. Another way of determining the nature of the termination consists in the identification of the termination product by chemical and spectroscopic methods.

It has been established unambiguously that heterocyclic and aliphatic† nitroxy-radicals, in particular radicals of the piperidine series having the general formula (I), react solely with the alkyl radicals $R^{\cdot}$ and do not interact with the peroxy-radicals $RO_2^{\cdot}$.

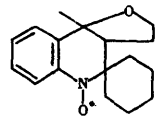


(I)
2,2,6,6-Tetramethylpiperidin-1-yloxy-radical



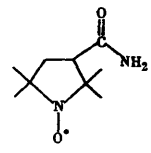
(II)
Diphenylnitroxy-radical

† All these non-aromatic radicals will henceforth be referred to for brevity simply as heterocyclic radicals.



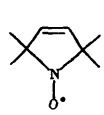
(III)

4-Methyl-2-spirocyclohexyl-3,4,2′,3′-tetrahydrofurano-1,2,3,4-tetrahydroquinolin-1-xyloxy-radical



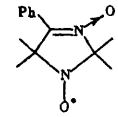
(IV)

3-Carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-yloxy-radical



(V)

2,2,5,5-Tetramethylpyrrolin-1-yloxy-radical



(VI)

2,2,5,5-Tetramethyl-4-phenyl-3-oxoimidazolin-1-yloxy-radical

This was demonstrated in the oxidation of ethylbenzene,[24,25] polyethylene and polypropylene,[26] and cumene and cyclohexyl methyl ether,[27] in the radiolysis of organic compounds,[28,29] and in the decomposition of azoisobutyrodinitrile.[30] It has been established that, in the radiolysis of water,[31] the nitroxy-radicals (VI) of the imidazoline series react with H atoms and with a hydrated electron but do not react with the $HO_2^{\cdot}$ radical. Fig.1 illustrates the reactivity of heterocyclic nitroxy-radicals. It is seen that, in an atmosphere of oxygen, where the $RO_2^{\cdot}$ radicals propagate the oxidation chain, the nitroxy-radical (I) is not consumed in the oxidation of ethylbenzene. The stationary concentration of the $RO_2^{\cdot}$ radicals, characterised by the chemiluminescence intensity (I/I_0), then also remains unchanged.

In the oxidation of many compounds, especially aromatic hydrocarbons, the stationary concentration of peroxy-radicals is much higher than the concentration of the alkyl radicals R$^{\cdot}$, as a result of which the heterocyclic nitroxy-radicals cannot be effective inhibitors of such reactions. On the other hand, in the oxidation of olefins characterised by relatively high concentrations of the radical R$^{\cdot}$, the inhibition of the reaction by heterocyclic nitroxy-radicals has been observed. As an illustration, Fig.2 presents the kinetic curves for the liquid-phase oxidation of hex-1-ene inhibited by a nitroxy-radical of type (I).[32] An analogous picture has been observed in the oxidation of β-carotene (a polyene).[33]

The interaction of heterocyclic nitroxy-radicals with alkyl radicals results in the formation of the corresponding hydroxylamine ethers:[29,34–36]

$$>NO^{\cdot} + R^{\cdot} \xrightarrow{k_a} >NOR \ .$$

The disproportionation reaction is also possible:

$$>NO^{\cdot} + R^{\cdot} \xrightarrow{k_b} >NOH + \text{olefin}.$$

According to Berger et al.,[30] the ratio $k_b/k_a = 0.21$ for the nitroxy-radical (I) and the radicals $(C_6H_5)_2\dot{C}(CH_3)$ and does not change over the range 60–80 °C. In the presence of hydrogen atoms in the α-position, a decomposition reaction can occur,[37,38] for example:

$$>NO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-R \rightarrow >NOH + R-CH=CH_2 \ .$$

In an acid aqueous medium, hydroxylamine ethers are capable of being deprotonated and of dissociating:[29]

$$>NOR + H^+ \rightarrow -\overset{+}{N}HOR \ ;$$

$$-\overset{+}{N}HOR \rightleftarrows >NOR + H^+_{aq} \ .$$

The pK_a for the equilibrium depends on the nature of the radical R and the nitroxy-radical.

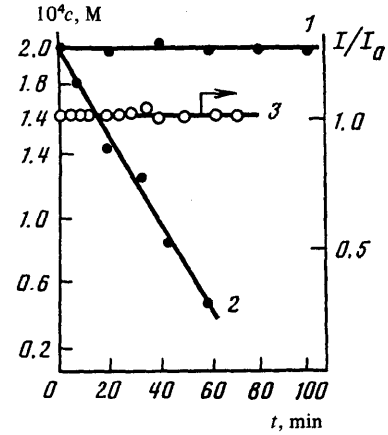


Figure 1. The time (t) variation of the concentration of type (I) nitroxy-radicals (c) in ethylbenzene at 60 °C with the solution bubbled with air (line *1*) and helium (line *2*) and variation of the relative intensity of chemiluminescence (line *3*) under the same conditions for the solution bubbled with air.[25]

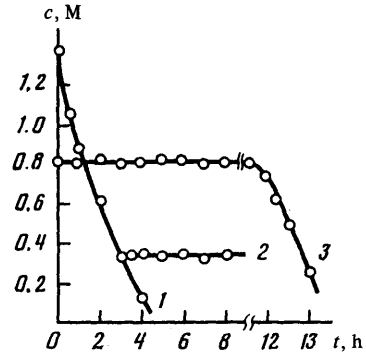
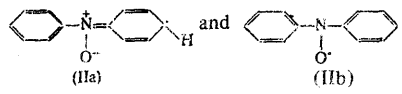


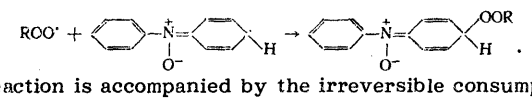
Figure 2. Kinetic curves for the consumption of hex-1-ene during its oxidation with air in acetone (145 °C, 50 atm):[32] 1) without inhibitor; 2) in the presence of 3×10^{-3} M 4-hydroxy derivative of the radical (I); 3) in the presence of 5.2×10^{-4} M 4-hydroxy derivative of the radical (I).

Aromatic nitroxy-radicals, for example, the radicals (II) of the diphenylamine series, can react not only with the radicals R$^{\cdot}$ but also with $RO_2^{\cdot}$. Nitroxy-radicals of type (II) can exist in two forms:[39,40]

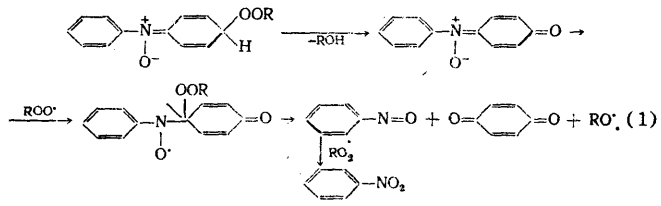


(IIa) (IIb)

The radicals $RO_2^{\cdot}$ are destroyed with participation of the mesomeric form (IIa), which can be represented as follows:[24,39]



This reaction is accompanied by the irreversible consumption of the nitroxy-radical via the mechanism:

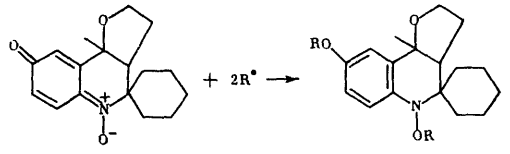


It has been suggested[41] that the nitroxy-radical (II) interacts with the $RO_2^{\cdot}$ radical as follows:

$$\rangle NO^{\cdot} + C_nH_{2n+1}O_2^{\cdot} \xrightarrow{k_b} \rangle NOH + O_2 + C_nH_{2n}. \quad (2)$$

When cumene is heated in the absence of oxygen but in the presence of an initiator, namely azobisisobutyrodinitrile (AIBN), the aromatic nitroxy-radical (II) reacts with the radicals $R^{\cdot}$, forming a hydroxylamine ether, as in the reaction involving heterocyclic nitroxy-radicals.

According to Lobanova and co-workers,[42,43] the spiran nitroxy-radical (III) also interacts not only with alkyl but also with peroxy-radicals. The quinone-nitrone formed in the latter case does not react further with $RO_2^{\cdot}$, but functions as an acceptor of alkyl radicals:



The nitroxy-radical (III) is capable of reacting also with alkoxy-radicals $RO^{\cdot}$, but the product formed has not been identified. On the other hand, it does not react with phenoxy-radicals.

The reactions of nitroxy-radicals with other free radicals, formed in the oxidation of alcohols and amines, are distinguished by certain characteristic features. Both "alkyl" and peroxy-radicals derived from alcohols and amines can be destroyed by any nitroxy-radicals[44,45] and the reaction product is not an ether but the corresponding hydroxylamine itself:

$$\rangle NO^{\cdot} + HO-\dot{C}\langle \rightarrow \rangle NOH + O{=}C\langle . \quad (3)$$

While the alcohol is converted into a carbonyl compound, the amine is converted into a Schiff base:

$$\rangle NO^{\cdot} + H_2N-\dot{C}\langle \rightarrow \rangle NOH + -N{=}C\langle . \quad (4)$$

Reactions of types (3) and (4) have been observed in an inert atmosphere for different heterocyclic nitroxy-radicals and the nitroxy-radical (II). The interaction of heterocyclic nitroxy-radicals with the peroxy-radicals formed in the oxidation of secondary and tertiary aliphatic amines has been described.[45,46] The peroxy-radicals are destroyed via the reaction:

$$-NH-\underset{|}{\overset{|}{C}}COO^{\cdot} + \rangle NO^{\cdot} \rightarrow \rangle NOH + -N{=}C\langle + O_2 . \quad (5)$$

The inhibition of the oxidation reactions can be achieved not only by the addition of complete nitroxy-radicals but also as a result of the introduction into the oxidation system of primary and secondary amines, which are capable of being converted into nitroxy-radicals under these conditions.[47-49] Thus in the presence of diphenylamine the following reactions take place:

$$(C_6H_5)_2NH + RO_2^{\cdot} \xrightarrow{k_c} (C_6H_5)_2N^{\cdot} + ROOH ; \quad (6)$$

$$(C_6H_5)_2N^{\cdot} + RO_2^{\cdot} \xrightarrow{k_d} (C_6H_5)_2NO^{\cdot} + RO^{\cdot} . \quad (7)$$

Nitroxy-radicals are usually not formed in the oxidation of tertiary amines.[47] The oxidation reactions of tertiary amines derived from indoline are an exception.[50]

In the oxidation of cumene, $k_d = 6 \times 10^3$ litre mol^{-1} s^{-1} at 57 °C [41] and $k_c = 4 \times 10^4$ litre mol^{-1} s^{-1} at 65 °C.[30] At the same temperature, $k_d > k_c$ according to Berger et al.[30] According to the data of Howard and Wiles,[51] the abstraction of a hydrogen atom from secondary aliphatic amines is much slower than the abstraction from aromatic amines.

Nitroxy-biradicals exhibit fundamentally the same inhibiting properties as the monoradicals. According to Brownlie and Ingold[52] and Ruban et al.,[53] the inhibition reaction is preceded by the decomposition of the biradical into the two corresponding monoradicals. The question of the reactivity of the nitroxy-biradicals and nitroxy-polyradicals has been discussed in detail.[2] Nitroxy-radicals can be introduced into the reaction also in an immobilised form. Thus polystyrene containing t-butylnitroxy-groups (one $\rangle NO^{\cdot}$ group per 250 to 300 monomer units) is an effective inhibitor of radical reactions.[54]

Taking into account the ability of nitroxy-radicals to interact with alkyl radicals, it is to be expected that they inhibit not only oxidation reactions but also other radical processes. Indeed they behave as inhibitors of polymerisation, especially of chloroprene, acrylates and methacrylates, vinyl monomers, styrene, etc.[1,54,55]

III. KINETIC CHARACTERISTICS OF NITROXY-RADICALS AS ANTIOXIDANTS

In order to be able to discuss the kinetic parameters characterising the inhibiting capacity of nitroxy-radicals, we shall make use of the general mechanism of the oxidation processes accompanied by polymerisation in the presence of nitroxy-radicals. This scheme is based on the available published experimental data:

Scheme I

$$RH \xrightarrow{O_2} R^{\cdot}, \quad (0)$$

$$R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot}, \quad (1)$$

$$RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot}, \quad (2)$$

$$ROOH \xrightarrow{k_3} RO^{\cdot}, OH, RO_2^{\cdot}, \quad (3)$$

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_4} \text{molecular products}, \quad (4)$$

$$R^{\cdot} + RO_2^{\cdot} \xrightarrow{k_5} \text{molecular products}, \quad (5)$$

$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_6} \text{molecular products}, \quad (6)$$

$$R^{\cdot} + \rangle NO^{\cdot} \xrightarrow{k_7} \rangle NOR, \quad (7)$$

$$RO_2^{\cdot} + \rangle NOR \xrightarrow{k_8} ROOR + \rangle NO^{\cdot}, \quad (8)$$

$$RO_2^{\cdot} + \rangle NOR \xrightarrow{k_9} \text{molecular products}, \quad (9)$$

$$RO_2^{\cdot} + \rangle NO^{\cdot} \xrightarrow{k_{10}} [RO_2^{\cdot} \cdots \rangle NO] \text{ or } \rangle NOH + \rangle C{=}C\langle + O_2 , \quad (10)$$

$$\rangle NO^{\cdot} + RH \xrightarrow{k_{11}} \rangle NOH + R^{\cdot} . \quad (11)$$

When the compound being oxidised contains C=C double bonds or when an unsaturated compound M is added to a saturated substance undergoing oxidation, the mechanism must be supplemented by the following reactions:

$$\rangle NO^{\cdot} + M^{\cdot} \xrightarrow{k_{12}} \text{molecular products}, \quad (12)$$

$$\rangle NO^{\cdot} + M \xrightarrow{k_{13}} M^{\cdot}, \quad (13)$$

$$M^{\cdot} + O_2 \xrightarrow{k_{14}} MO_2^{\cdot}, \quad (14)$$

$$MO_2^{\cdot} + M \xrightarrow{k_{15}} M^{\cdot}, \quad (15)$$

$$MO_2^{\cdot} + MO_2^{\cdot} \xrightarrow{k_{16}} \text{molecular products}. \quad (16)$$

Here R$^{\cdot}$ is an alkyl radical, $\rangle NO^{\cdot}$ the nitroxy-radical, and M the olefin molecule.

Apart from the usual reactions characteristic of the non-inhibited chain oxidation process,[56] the scheme includes stages involving the destruction of free radicals by the nitroxy-radical [reactions (7), (9), (10), and (12)] and the regeneration of the nitroxy-radicals from their reaction products [reaction (8)]. Reactions (11) and (13) refer to the initiation of free radical chains by the nitroxy-radicals as a result of their addition to the double bond or the abstraction of a hydrogen atom from the molecule of the organic substrate. All these reactions will be discussed in greater detail below.

The efficiency of nitroxy-radicals as oxidation inhibitors can be characterised very approximately by measuring the induction period. Naturally, when different nitroxy-radicals are compared, the determination must be carried out with identical amounts of the inhibitor and under the same experimental conditions. In particular, by measuring the induction periods, it has been established that nitroxy-radicals derived from quinoline and carboline are less effective inhibitors of the oxidation of polypropylene and of the oxidative degradation of polyformaldehyde than the nitroxy-radicals of type (I).[57] The antioxidant efficiencies of 15 nitroxy-radicals having different structures have been characterised[55] from the induction periods in the oxidation of polypropylene. It is of interest that the induction period in the oxidation of polypropylene[55,58] continues even after the apparent consumption of the nitroxy-radicals, i.e. after the disappearance of the corresponding EPR signal. One can therefore assume that in certain systems the nitroxy-radical behaves as an inhibitor even at very low stationary concentrations in the system—below the sensitivity limit of the EPR method.

The inhibiting capacity of nitroxy-radicals is characterised much more accurately by the rate constants for the elementary stages of the inhibition process. When alkyl radicals are destroyed by a nitroxy-radical, the rate constant k_7 or the ratio k_1/k_7 is usually determined.[25,27,51] The rate constants k_{10} for type (II) nitroxy-radicals have been measured in the oxidation of ethylbenzene and styrene. The study of the inhibited oxidation of alcohols and amines yielded the combinations of rate constants $k_{10}/k_6^{1/2}$ for nitroxy-radicals of different structure. The rate constant k_{10} refers in this instance to a disproportionation reaction of type (5) and not to the recombination of radicals.

A novel method of characterising nitroxy-radicals as inhibitors has been proposed.[59] In contrast to the traditional approach requiring the comparison of the rates of chain propagation [reaction (1)] and chain termination by the nitroxy-radical [reaction (7)] in Scheme 1, here the rates of chain termination were compared in the presence and absence of the nitroxy-radical. An expression was then obtained for the minimum concentration of the nitroxy-radical necessary for the inhibition of the oxidation of the organic compound RH:

$$\left[\rangle NO^{\cdot}\right]_{min} > \frac{k_1\sqrt{W_0 k_6}\,[O_2]}{k_5 k_7\,[RH]}, \quad (8)$$

where W_0 is the rate of chain initiation in reaction (0) in Scheme 1.

Table 1. Kinetic parameters of the reactions of nitroxy-radicals with organic free radicals (the designations correspond to the numbering of the reactions in Scheme 1 and to the numbering of the nitroxy-radicals—see the beginning of the review).

Source of hydrocarbon radicals	Nitroxy-radical	T, °C	Value of parameter	Refs.
	k_7, litre mol^{-1} s^{-1}			
Styrene	4-Hydroxy-(I) and 4,4'-dimethoxy-(II)	50	$2.1\cdot10^4$	[53]
"	2,2',6,6'-Tetramethyl-4,4'-dimethoxy-(II)	50	$2.8\cdot10^4$	[53]
"	2,2'4,4'-Tetramethoxy-(II)	50	$3.2\cdot10^4$	[53]
Polystyrene	4-Oxo-(I)	65	10^7	[52]
Styrene	4,4'-Diethoxy-(II)	70	$2.7\cdot10^5$	[88]
"	4,4'-Diisopropyl-(II)	60	$1.4\cdot10^5$	[89]
"	4-Hydroxy-(I)	60	$2.0\cdot10^5$	[89]
"	4,4'-Dimethoxy-(II)	60	$1.7\cdot10^5$	[89]
Methylacrylate	(I)	50	$3.0\cdot10^7$	[90]
Methyl methacrylate	(I)	50	$1.2\cdot10^7$	[90]
Ditto	3-Cyano-(V)	50	$2.0\cdot10^7$	[90]
"	4-Hydroxy-(I)	50	$8.0\cdot10^6$	[90]
Isobutyl methacrylate	(I)	50	$9.0\cdot10^6$	[90]
Methanol	4-Oxo-(I)	25*	$7.2\cdot10^8$	[28]
"	3-Carbamoyl-(V)	25	$4.6\cdot10^8$	[29]
"	(VI)	25	$3.5\cdot10^8$	[29]
Ethanol	4-Oxo-(I)	25	$6.4\cdot10^8$	[28]
"	(VI)	25	$6\ 2\cdot10^8$	[29]
Isopropyl alcohol	4-Oxo-(I)	25	$3.9\cdot10^8$	[28]
Ditto	(VI)	25	$3.6\cdot10^8$	[29]
Methane	3-Carbamoyl-(V)	25	$7.5\cdot10^8$	[29]
"	(VI)	25	$7.8\cdot10^8$	[29]
Cyclopentane	3-Carbamoyl-(V)	25	$3.5\cdot10^8$	[29]
"	(VI)	25	$3.6\cdot10^8$	[29]
Reaction with				
e^-	4-Oxo-(I)	25	$2.2\cdot10^9$	[28]
e^-	3-Carbamoyl-(V)	25	$9.0\cdot10^9$	[29]
e^-	(VI)	25	$1.9\cdot10^{10}$	[29]
H	4-Oxo-(I)	25	$5.7\cdot10^9$	[28]
H	3-Carbamoyl-(V)	25	$5.3\cdot10^9$	[29]
H	(VI)	25	$6.9\cdot10^9$	[29]
OH	4-Oxo-(I)	25	$<10^8$	[28]
OH	3-Carbamoyl-(V)	25	$3.7\cdot10^9$	[29]
OH	(VI)	25	$5.4\cdot10^9$	[29]
	k_{10}, litre mol^{-1} s^{-1}			
Ethylbenzene	4,4'-Dimethoxy-(II)	70	$1.2\cdot10^6$	[2]
"	"	60	$6.0\cdot10^5$	[25]
Cyclohexyl methyl ether	"	75	$2.4\cdot10^3$	[27]
Cumene	(II)	68	$2.5\cdot10^3$	[41]
Styrene	4,4'-Dimethoxy-(II)	65	$5.0\cdot10^4$	[52]
Cyclohexylamine	4-Hydroxy-(I)	75	$2.7\cdot10^7$	[92]
Di(n-butyl)amine	"	75	$1.5\cdot10^8$	[92]
Cyclohexanol	"	75	$2.2\cdot10^8$	[92]
Dimethylaminoethylmethacrylate	"	30—60	$10^{8.2}\exp(-2700/RT)$	[90]
Ditto	"	50	$8.2\cdot10^3$	[90]
Dimethylaminoethyl propionate	"	50	$3.0\cdot10^3$	[90]
Dimethylbutylamine	"	50	$5.6\cdot10^4$	[90]
	k_1/k_7			
Cumene	(I)	60	18	[27]
"	4-Hydroxy-(I)	60	29.5	[93]
Polypropylene	"	85	0.4	[93]
Cyclohexyl methyl ether	(I)	75	3.1	[27]
Styrene	4-Oxo-(I)	65	10	[52]
Ethylbenzene	"	60	26	[25]
n-Octane**	"	0	0.6	[94]
"	"	100	7.7	[94]
"	4-Hydroxy-(I)	100	6.2	[94]
	$k_{10}/k_6^{1/2}$, litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$			
Cyclohexylamine***	(I)	75	5.4	[45]
"	(VI)	75	4.5	[45]
"	4,4'-Dimethoxy-(II)	75	18	45
Di-n-butylamine	(I)	75	21	[45]
"	(VI)	75	10	[45]
"	4,4'-Dimethoxy-(II)	75	32	[45]
Cyclohexanol	4-Hydroxy-(I)	75	125	[45]
"	(VI)	75	34	[45]
"	4,4'-dimethoxy-(II)	75	48	45]
	k'_b, litre mol^{-1} s^{-1}			
Azobisisobutyrodinitrile	Quinone-nitrone obtained from the nitroxy-radical (III)	50	$8\cdot10^3$	[43]

*During pulsed radiolysis.
**Radiation-chemical oxidation (^{60}Co γ-radiation).
***$E_{10}-\frac{1}{2}E_6 = 3.0$ kcal mol^{-1} at 65–85 °C.

Eqn.(8), which relates the minimum concentration of nitroxy-radicals necessary for the complete arrest of the reaction to the principal kinetic parameters of the system, can be used to determine the constant k_7 by measuring $[\rangle NO^{\cdot}]_{min}$.

The available literature data for the kinetic parameters of the interaction of nitroxy-radicals with free radicals are presented in Table 1.

When nitroxy-radicals are used as inhibitors, one must bear in mind that they can participate in free radical formation reactions. Nitroxy-radicals are hardly involved in chain branching via interaction with the hydroperoxide formed in the oxidation process, which has been demonstrated, for example, in the study of the decomposition of propene hydroperoxide.[24] However, in the presence of certain catalysts, nitroxy-radicals can accelerate the decomposition of hydroperoxides. Thus the promoting effect of the nitroxy-radical (I) in the decomposition of tetralinyl and cyclohexyl hydroperoxides in the presence of copper-containing catalysts has been established.[60,61] The effect of nitroxy-radicals can be attributed to the formation of a complex with the catalyst. In particular, it is known that they are capable of forming complexes with univalent and bivalent copper.[62] An interesting observation has been made in the study of the kinetics of the decomposition of peroxide initiators—benzoyl peroxide[63] and dicyclohexyl peroxydicarbonate[64]—in the presence of nitroxy-radicals. It was established that, in the absence of catalysts, nitroxy-radicals are able to accelerate the decomposition of peroxide compounds, provided that the concentration of the nitroxy-radical in the system is comparable to that of the peroxide.

On the other hand, nitroxy-radicals can generate free radicals by abstracting a hydrogen atom from the molecule of the organic compound [reaction (11)] or by adding to the double bond [reaction (13) in Scheme 1]. The importance of the latter reaction also lies in the fact that nitroxy-radicals have found a practical application as inhibitors of the polymerisation of unsaturated compounds. Reaction (11) has been investigated in ethylbenzene,[65] toluene,[66] phenylhydrazones,[67] di-t-butylphenol,[68] hydrazobenzene,[69] and mercaptans.[70] Reaction (13) has been investigated only for styrene and heterocyclic nitroxy-radicals.[71–73] In the case of α-methylstyrene, where the reaction involved the participation of monoradicals, addition to the double bond was not observed even at 180 °C. However, under the same conditions, the nitroxy-biradical adds readily to α-methylstyrene. This difference between reactivities can be accounted for by the greater probability for the biradical of the adiabatic reaction pathway characterised by a low activation energy.[2] The rate constants for reactions (11) and (13) are presented in Table 2.

Taking into account the possibility of the initiation by free radicals via reaction (13) in Scheme 1, we shall estimate the optimum amounts of the nitroxy-radical necessary for the inhibition of the oxidation of hydrocarbons via Scheme (1) presented above. If the compound oxidised RH has no double bond, it is assumed that an unsaturated compound, which is a source of additional initiation, constitutes a second component of the oxidation system. An increase in the induction period with increased concentration of the nitroxy-radical has been observed experimentally, but at sufficiently high concentrations it ceases to change. This can be explained by the fact that the rate of initiation by the nitroxy-radical

Table 2. The rate constants for the reactions of nitroxy-radicals leading to the formation of free radicals.

Substrate	Nitroxy-radical	T, °C	Value of constant, litre mol^{-1} s^{-1}		Refs.
			k_{13}	k_{11}	
Ethylbenzene	4-Oxo-(I)	100—200	—	$1.2\cdot10^{3}\exp(-15\,400/RT)$	[65]
"	4,4'-Dimethoxy-(II)	100—200	—	$1.1\cdot10^{3}\exp(-14\,500/RT)$	[65]
"	4,4'-Dinitro-(II)	100—200	—	$9.6\cdot10^{3}\exp(-24\,800/RT)$	[65]
"	(II)	100—200	—	$7.8\cdot10^{5}\exp(-19\,100/RT)$	[65]
Styrene	(I)	105—120	$6\cdot10^{4}\exp(-17\,000/RT)$	—	[71]
"	4-Oxo-(I)	105	$7\cdot10^{-4}$	—	[71]
"	Biradical*	105	10^{-5}	—	[71]
α-Methylstyrene	"		$6\cdot10^{3}\exp(-15\,000/RT)$	—	[71]
Hydrazobenzene	4-Oxo-(I)	20—72**	—	$7.2\cdot10^{3}\exp(-5\,000/RT)$	[69]
"	(I)	20—72	—	$4.1\cdot10^{3}\exp(-5\,000/RT)$	[69]
"	4-Hydroxy-4-ethyl-(I)	20—72	—	$2.3\cdot10^{3}\exp(-5\,000/RT)$	[69]
"	3-Formyl-(V)	20—72	—	$58\exp(5\,000/RT)$	[69]
Styrene	4-Benzoyl-(I)	60	$3.7\cdot10^{-6}$	—	[72]
"	(I)	80	10^{-5}; $2.2\cdot10^{-5}$***	—	[73]
4-Methyl-2,6-di-t-butyl-methylenequinone	4-Hydroxy-(I)	20—60	$1.6\cdot10^{3}\exp(-29\,000/RT)$	—	[95]
Raw rubber	(I)	90—130	—	$10^{8}\exp(-18\,000/RT)$	[80]
Non-1-ene	4-Benzoyl-(I)	120	$<10^{-5}$	—	[91]
β-Carotene	(I)	50	$4.0\cdot10^{-4}$	—	[33]
Cetane	4-Oxo-(I)	190—220	—	$5.2\cdot10^{10}\exp(-36\,000/RT)$	[96]
"	(III)	160—194	—	$1.7\cdot10^{5}\exp(-23\,000/RT)$	[96]
Silane****	4-Oxo-(I)	150—182	—	$6.0\cdot10^{11}\exp(-34\,000/RT)$	[96]
"	(III)	110—145	—	$9.6\cdot10^{6}\exp(-21\,500/RT)$	[96]
"	4,4'-Dimethoxy-(II)	85—115	—	$4.5\cdot10^{8}\exp(-23\,500/RT)$	[96]

*The biradical $ROOC(CH_2)_4COOR$, where R is the radical residue from the nitroxy-radical (I).

**The activation energies are almost identical for all the nitroxy-radicals.

***At a pressure of 2000 atm.

****The silane is



becomes higher than the rate of thermal initiation. The induction period is given by

$$\tau = \frac{p}{k_2} \cdot \frac{k_7 \left[\rangle NO^{\cdot}\right]}{W_0 + k_{13}\left[\rangle NO^{\cdot}\right][M]} ,$$

where p is the fraction of the substrate which has reacted at the instant when the induction period ends. At the nitroxy-radical concentration corresponding to the start of the region of constant τ, we have

$$k_{13}\left[\rangle NO^{\cdot}\right][M] \gg W_0 ;$$

whence

$$\tau = \frac{pk_7}{k_2 k_{13}[M]} . \qquad (9)$$

The rate of the oxidation process is then given by

$$W = k_2 k_{13}[RH][M]/k_7$$

Eqn.(9) describes the region where the induction period is independent of the concentration of the nitroxy-radical. The optimum concentration of the nitroxy-radical, corresponding to the region of the independence of the induction period, is

$$\left[\rangle NO^{\cdot}\right]_{opt} = W_0/k_{13}[M] .$$

An increase in the concentration of the nitroxy-radical above $[\rangle NO^{\cdot}]_{opt}$ is undesirable, since it does not lead to a further increase of the induction period. Calculation of the quantity $[\rangle NO^{\cdot}]_{opt}$ may be of practical value when nitroxy-radicals are used for the antioxidant stabilisation of materials containing double bonds. The parameter characterising the inhibiting efficiency of nitroxy-radicals under the conditions of significant additional initiation can be deduced from Eqn.(9):

$$K = k_7/k_2k_{13}$$

IV. THE INHIBITION COEFFICIENT AND REGENERATION OF NITROXY-RADICALS

One of the most important characteristics of the inhibitors of radical processes, including nitroxy-radicals, is the stoichiometric inhibition coefficient f. The integral definition, according to which f is equal to the number of free radicals destroyed by one inhibitor molecule, is widely used in the chemical literature:

$$f \cdot [InH]_0 = W_0\tau ,$$

where $[InH]_0$ is the initial inhibitor concentration. A method of determining f in the case of weak inhibitors which do not give rise to a distinct induction period has been described.[39]

However, in the integral definition no account is taken of the fact that f depends on the ratio of the rates of the individual elementary stages of the inhibition process. The role of this ratio is evident from the following simple example. In a system containing the free radicals R$^{\cdot}$ to which the inhibitor InH has been introduced, two radical destruction reactions can take place:

$$R^{\cdot} + InH \rightarrow RH + In^{\cdot} , \qquad (10)$$

$$R^{\cdot} + In^{\cdot} \rightarrow RIn . \qquad (11)$$

Even in this case the quantity f depends on the ratio of the rates of reactions (10) and (11). If the rate of reaction (11) greatly exceeds that of reaction (10), then $f = 2$. In the opposite case $f = 1$ and for comparable rates of the two reactions we have $1 < f < 2$.

A differential, i.e. "rate" treatment of the quantities f for the reactions involving inhibition by nitroxy-radicals has been described.[59] In this case the expression for f represents the ratio of the sum of the rates of the elementary stages in which the chain propagating free radicals are destroyed to the sum of the rates of the elementary stages in which the inhibitor is consumed. According to Scheme 1,

$$f = \frac{1 + \beta\left[\rangle NOR\right]/\left[\rangle NO^{\cdot}\right]}{1 - \{k_8/(k_8 + k_9)\} \cdot \beta \cdot \left[\rangle NOR\right]/\left[\rangle NO^{\cdot}\right]} , \qquad (12)$$

where

$$\beta = \frac{(k_8 + k_9)[RO_2^{\cdot}]}{k_7[R^{\cdot}]} = \frac{(k_8 + k_9)k_1[O_2]}{k_2k_7[RH]} .$$

The rate of change of the concentration of $\rangle NOR$—the product of the reaction of the initial nitroxy-radical—in the course of the oxidation process is described by the expression

$$d\left[\rangle NOR\right]/dt = k_7[R^{\cdot}]\left[\rangle NO^{\cdot}\right] - (k_8 + k_9)[RO_2^{\cdot}]\left[\rangle NOR\right] .$$

The rearrangement of this equation and integration using the approximation $[RO_2^{\cdot}] = [\overline{RO_2^{\cdot}}]$, i.e. for the average concentration of the radicals $RO_2^{\cdot}$ in the course of the entire process, lead to the expression

$$\frac{\left[\rangle NOR\right]}{\left[\rangle NO^{\cdot}\right]} = \frac{1}{\beta}(1 - e^{-\beta t/t_c}) . \qquad (13)$$

The time during which the rates of formation and consumption of the product $\rangle NOR$ become equal is

$$t_c = 2/(k_8 + k_9)[\overline{RO_2^{\cdot}}] = 2(\beta W_0)^{-1}\left[\rangle \overline{NO^{\cdot}}\right] .$$

Comparison of Eqns.(13) and (12) shows that, when $t = t_c$, the ratio $[\rangle NOR]/[\rangle NO^{\cdot}]$ is close to $1/\beta$. During the reaction, the quantity f changes from 1 at the beginning of the oxidation to $2[1 + (k_8/k_9)]$. Estimation of the parameters β and t_c using the known rate constant k_7, k_{14},[48] k_8,[24,32] and k_{15}[74] leads to $\beta = 10^{-3}$–10^{-2} and $t_c = 10^4$–10^5 s. For short reaction times (up to 3–4 h), the condition $t = t_c$ is not attained and f continuously increases during the reaction without reaching, however, its maximum value.

According to Vardanyan et al.,[75] the inhibition coefficient in oxidation inhibited by amines is defined by the equation

$$f = 2(k_8 + k_9)/k_9 . \qquad (14)$$

This expression is a special case of Eqn.(12) and is valid for systems where $k_8 \gg k_7$, i.e. the time required for the attainment of a stationary concentration of the inhibitor reaction product is much shorter than the duration of the oxidation reaction. In studies of the oxidation of polypropylene,[26,76] it has been stated that f increases with increase of oxygen concentration in the system. Indeed an increase in the O_2 concentration increases the efficiency of the inhibition by the nitroxy-radical as a result of the decrease of t_c. On the other hand, the maximum value of f, defined by Eqn.(14), is independent of the oxygen concentration.

The high absolute values of f under conditions where nitroxy-radicals are used in oxidation processes are caused by the inhibitor regeneration reaction [reaction (8) in Scheme (1)] and the increase of f during the process is associated with the increase of its rate as the primary product of the interaction of the nitroxy-radical with the alkyl radical R$^{\cdot}$ accumulates. The increase of f naturally leads to a decrease of the apparent rate of consumption of the nitroxy-radical

during the oxidation process. The inhibition coefficients in different systems are listed in Table 3.

Table 3. The inhibition coefficients (f) of nitroxy-radicals.

Nitroxy-radical	Substrate oxidised	f	Refs.
p-Ethoxy-(II)	Liquid paraffin	28	[39]
4,4'-Dinitro-(II)	Ditto	15	[39]
(I)	"	510	[39]
4-Oxo-(I)	"	410	[39]
Di-t-butylnitroxy-radical	"	225	[39]
4-Benzoyl-(I)	"	630	[39]
"	n-Hexylbenzene	3900	[30]
"	ββ-Dideuterio-n-hexylbenzene	1100	[30]
(I)	Liquid paraffin + 10 wt.% of diphenylmethane	190	[30]
(I)	Liquid paraffin + 10 wt.% of 1,1-diphenylethane	580	[30]
4-Oxo-(I)	n-Hexylbenzene	720	[30]
(I)	Cyclohexa-1,3-diene	90	[77]
4-Oxo-(I)	Tri-n-butylamine	40	[46]
4-Hydroxy-(I)	Benzaldehyde	100	[78]
"	Acetaldehyde + styrene	20	[59]

In particular, it follows from Table 3, that in the oxidation of higher paraffins, $f = 15$–35 for aromatic nitroxy-radicals, 225 for the aliphatic t-butylnitroxy-radical, and 500–600 for heterocyclic nitroxy-radicals. The observed difference between the values of f is apparently associated with the fact that aromatic nitroxy-radicals readily enter into side reactions, which lead to their irreversible consumption [reaction (1)].

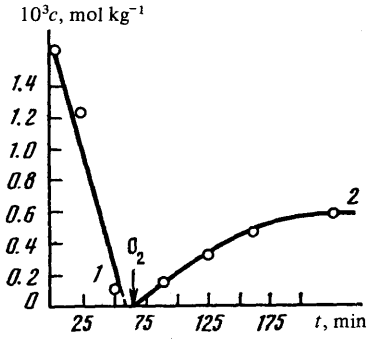


Figure 3. Kinetic curves for the consumption of the 4-hydroxy-derivatives of the nitroxy-radical (I) in an atmosphere of argon (curve *1*) and for the accumulation of the nitroxy-radical after the admission of oxygen (curve *2*) in isotactic polypropylene at 114 °C.[27]

The idea that the regeneration reaction (8) is in fact responsible for the high values of f is nowadays generally accepted. The occurrence of this reaction is convincingly indicated by the available experimental data. In an inert atmosphere, nitroxy-radicals interact with organic free radicals generated in the system, which results in the complete consumption of the nitroxy-radicals. When oxygen is passed subsequently through the reaction mixture, nitroxy-radicals reappear and their concentration increases to a stationary value (Fig.3). In particular, such regeneration has been observed in the interaction of nitroxy-radicals and nitroxy-biradicals with the products of the radiation-chemical reactions of n-octane[35] and the photochemical reactions of rubber[75] and also in the decomposition of the initiator AIBN in polypropylene,[76] aliphatic alcohols, and amines.[45]

A detailed study has been made of the kinetics of certain reactions which can, in principle, lead to the generation of nitroxy-radicals.[27] Apart from the primary reaction (8) in Scheme 1 already mentioned, the following reactions were also investigated:

$$\rangle\mathrm{NOR} \xrightarrow{k_e} \mathrm{R}^{\cdot} + \rangle\mathrm{NO}^{\cdot}, \qquad (15)$$

$$\rangle\mathrm{NOR} + \mathrm{O_2} \xrightarrow{k_f} \rangle\mathrm{NO}^{\cdot} + \text{products}. \qquad (16)$$

The rate constants for different regeneration reactions are listed in Table 4. The data presented confirm the conclusion that reaction (8) is the main process responsible for the regeneration of nitroxy-radicals from their reaction products.

Table 4. The rate constants for the regeneration of nitroxy-radicals from hydroxylamine ethers.

Ether $\rangle$NOR	T, °C	Value of parameter	Refs.
	k_e, s		
O-1,1-Diphenylethyl-4-oxo-(I)	20—50	$10^{14.8}\exp(-24\,500/RT)$	[37]
"	50	$1.6\cdot10^{-5}$	[37]
O-Methyl-(I)	100	10^{-7}	[27]
O-Cyclohexyl-(I)	100	10^{-7}	[27]
O-t-butyl-(I)	100	$1.5\cdot10^{-5}$	[27]
O-Dimethylcyanomethyl-(I)	65—87	$10^{12.6}\exp(-25\,000/RT)$	[27]
"	100	$1.6\cdot10^{-2*}$	—
NNO-Tri-t-butylhydroxyl-amine	60—100	$1.2\cdot10^{9}\exp(-22\,900/RT)$	[30]
"	100	$5.8\cdot10^{-5}$	[30]
	k_f, litre mol^{-1} s^{-1}		
O-t-butyl-(I)	110	$5.0\cdot10^{-4}$	[27]
O-methyl-(I)	110	$5.0\cdot10^{-4}$	[27]
	k_8, litre mol^{-1} s^{-1}		
Bi-[*O*-cyclohexyl-(I)] (from the biradical)	100	$3.0\cdot10^{2**}$	[35]
O-Phenyl-(I)	65	1.0***	[27]
O-Ethyl-(I)	65	8.0***	[27]
O-Cyclohexyl-(I)	65	26.0***	[27]
O-t-Butyl-(I)	65	4.0***	[27]
NNO-tri-t-butylhdyroxyl-amine	100	44****	[30]

*Obtained by extrapolation.
**$RO_2^{\cdot}$ = n-$C_8H_{17}OO^{\cdot}$.
***$RO_2^{\cdot}$ = $(CH_3)_2CNOO^{\cdot}$.
****$RO_2^{\cdot}$ = $(CH_3)_2CHC_6H_4$-*p*-$C(CH_3)_2$–$OO^{\cdot}$.

The regeneration of nitroxy-radicals can apparently proceed not only with participation of the peroxy-radicals $RO_2^{\cdot}$ but also in the interaction with the oxy-radicals $RO^{\cdot}$. However in real oxidation systems the $RO_2^{\cdot}$ concentration usually exceeds by two orders of magnitude the $RO^{\cdot}$ concentration, as a result of which the main regenerating agent is in fact the peroxy-radical. In the styrene–acetaldehyde binary system, the type (I) nitroxy-radical is consumed at the same rate as in the oxidation of styrene alone,[59] which shows that the regeneration is effected by the peroxy-radicals derived from styrene, whose concentration is much higher than the concentration of acetyl peroxy-radicals. According to Vardanyan and Denisov,[77] the radicals $HO_2^{\cdot}$ are also capable of regenerating nitroxy-radicals.

It has been suggested[48] that the regeneration is caused by the hydroperoxide:

$$ROOH + \rangle NOH \rightarrow RO^{\cdot} + \rangle NO^{\cdot} + H_2O \ .$$

However, the available experimental data do not allow one to rule out the possibility that the nitroxy-radical is regenerated by the free radicals which can be formed from the hydroperoxide. The regeneration of nitroxy-radicals in an inert atmosphere under the influence of polymers subjected to prior oxidation has been investigated.[26] The oxidised polymer contains hydroperoxy-groups, which the authors[26] believe decompose with formation of the radicals RO$^{\cdot}$ responsible for the regeneration of the nitroxy-radical.

The peroxy-radicals $RO_2^{\cdot}$ are capable of regenerating the nitroxy-radical not only from the ethers but also from the hydroxylamine itself:[80]

$$\rangle NOH + RO_2^{\cdot} \rightarrow \rangle NO^{\cdot} + ROOH \ .$$

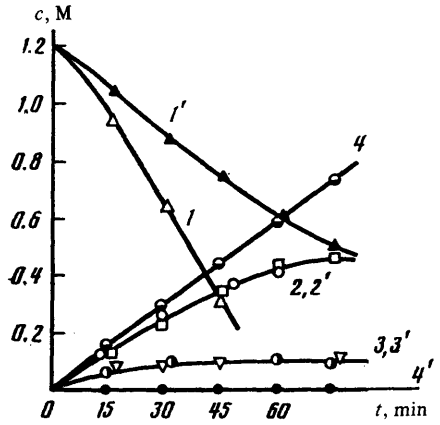


Figure 4. Kinetic curves for the consumption of styrene (curve *1*) and the accumulation of benzaldehyde (curve *2*), styrene oxide (curve *3*), and a polymeric product (curve *4*) in the coupled oxidation of styrene and acetaldehyde by air in benzene (70 °C, 50 atm); the primed numbers designate the corresponding curves in the presence of 2.2×10^{-3} M 4-hydroxy-derivative of the nitroxy-radical (I).[59]

The formation of hydroxylamines and the above regeneration mechanism have been observed mainly for chain termination resulting from the interaction with nitroxy-radicals having labile hydrogen atoms (for example, in the oxidation of alcohols or amines). In this cast too, the regeneration by the radicals $RO_2^{\cdot}$ takes place at a higher rate than in the interaction with O_2 or with the hydroperoxide. It is noteworthy that the rate of regeneration of the nitroxy-radical from hydroxylamines is higher than from their ethers. The regeneration of nitroxy-radicals from hydroxylamine ethers as a result of the abstraction of a hydrogen atom in the β-position is also possible:

$$R^1CH_2CH_2ON\langle + RO_2^{\cdot} \rightarrow \rangle NO^{\cdot} + R^1CH{=}CH_2 + ROOH \ .$$

The regeneration phenomenon must also be taken into account in those cases where the nitroxy-radicals are used to determine the rate of chain initiation W_0. In order to obtain the true values of W_0, it is essential to have accurate information about the inhibition coefficient in each specific case. On the other hand, the measurement of the rate of consumption of nitroxy-radicals in an inert atmosphere constitutes an extremely convenient method for the study of the kinetics of the decomposition of radical process initiators,[41,44,76] in particular the study of solvent cage effects in the decomposition process.[81] Nitroxy-radicals can be used as radical counters, for example in radiolytic processes[82] and in the determination of sulphur-containing radicals.[83]

In a study[84] of the oxidation of β-carotene (a polyunsaturated hydrocarbon) in the presence of the nitroxy-radical (III), it was shown that the observed high inhibition coefficients are related to an unusual type of regeneration—a relay process. In this instance, the regeneration effect is due to the "relay" radical reaction of the nitroxy-radical and its reaction products, which interact alternately with peroxy- and alkyl radicals derived from the substrate. An essential condition for such relay chain termination by the nitroxy-radical is a definite ratio of the concentrations of the alkyl and peroxy-radicals in the system:

$$10^{-3} - 10^{-2} \leqslant [R^{\cdot}]/[RO_2^{\cdot}] \leqslant 10^{-1} \ .$$

However, one should note that the nitroxy-radicals cannot evidently be regenerated in all cases from the reaction products. This is indicated by the finding that $f = 1$ is observed also for nitroxy-radicals in a number of instances, for example, in the oxidation of cumene.[41]

V. CHEMICAL REGULATION OF OXIDATION PROCESSES WITH THE AID OF NITROXY-RADICALS

In our investigations under the supervision of Emanuel' and with participation of Blyumberg and Tavadyan, it was established that nitroxy-radicals can be used to regulate the composition of the products in the oxidation of organic compounds. This possibility is associated with the phenomenon of the selective inhibition of many-centre chain processes, first described by Maslov and co-workers.[85,86] When the nitroxy-radical (I) was introduced into the coupled oxidation reaction of acetaldehyde and styrene[85] or of acetaldehyde and allyl chloride,[86] an appreciable increase in selectivity of the formation of monomeric oxygen-containing products was observed. In the absence of the nitroxy-radical, most of the initial unsaturated compound was converted into a polymeric product. Thus, in the case of styrene, an increase of selectivity with respect to monomeric products from 50 to 95 mole % and in the case of allyl chloride from 35 to 70 mole % was achieved.

The acetaldehyde–styrene binary oxidation system was selected for the detailed investigation of the mechanism of the selective inhibition by nitroxy-radicals. The conditions for selective inhibition, which will be briefly discussed below, were selected in relation to this system.[59] The kinetic curves for the coupled oxidation of styrene and acetaldehyde are illustrated in Fig.4. Examination of the experimental data permits the conclusion that in the system investigated there are two reaction chain carriers—the acetylperoxy-radicals RCOOO$^{\cdot}$ and the polyperoxy-radicals $MO_2^{\cdot}$ (M = styrene molecules), which propagate two independent process pathways—monomeric and polymeric respectively. This claim is supported in particular by the absence of dependence of the rate of accumulation of the monomeric products on the presence of nitroxy-radicals in the system. The existence of a definite

nitroxy-radical concentration at which the radicals do not inhibit the oxidation of the aldehyde but fully inhibit the formation of polymeric products, indicates the independence of the concentration of the radicals RCOOO· or the concentration of the radicals $MO_2^{\cdot}$, i.e. a negligibly low rate of the radical "exchange" reaction

$$MO_2^{\cdot} + RCHO \xrightarrow{O_2} RCOOO^{\cdot} + MOOH \ .$$

In this case the addition of the radicals RCOOO· to the double bond of the monomer is in essence a reaction involving the destruction of the chain in the monomeric reaction pathway:

$$RCOOO^{\cdot} + M \xrightarrow{k_g} M^{\cdot} \qquad (17)$$

Taking into account the simultaneous occurrence in the system of two independent processes, one may conclude that, as a result of reaction (12) (see Scheme 1), the nitroxy-radical reduces the concentration of the radicals $MO_2^{\cdot}$ without affecting the stationary concentration of RCOOO·. The appreciable change in the ratio of the concentrations of the radicals propagating different process pathways in favour of RCOOO· leads to the observed increase of the selectivity of the reaction with respect to monomeric products.

The presence of the induction period caused by the introduction of the nitroxy-radical indicates the fulfillment of the condition $W_7 \gg W_{17}$: on the other hand, at the end of the induction period $W_{17} > W_7$. The rate of reaction (12) should then exceed the rate of reaction (16) (in Scheme 1), which is a condition for the inhibition of the polymeric process pathway, i.e.

$$k_7[RCO^{\cdot}]\left[\rangle NO^{\cdot}\right] < k_g\,[RCOOO^{\cdot}]\,[M] \ ,$$

$$k_{12}\,[M^{\cdot}]\left[\rangle NO^{\cdot}\right] > k_{16}\,[MO_2^{\cdot}]^2 \ .$$

Bearing in mind that, during the occurrence of the chain propagation reactions

$$RCOOO^{\cdot} + M \xrightarrow{k_h} H_2C\!\!-\!\!\overset{O}{\overset{\diagup\diagdown}{}}\!\!-\!\!CH\!-\!C_6H_5 + RCOO^{\cdot} \ , \qquad (18)$$

$$RCOOO^{\cdot} + M \xrightarrow{k_i} C_6H_5CHO + RCOO^{\cdot} + HCHO \ , \qquad (19)$$

we have

$$\frac{[RCOOO^{\cdot}]}{[RCO^{\cdot}]} = \frac{k_1[O_2]}{(k_h + k_i)[M]}; \quad \frac{[MO_2^{\cdot}]}{[M^{\cdot}]} = \frac{k_{14}[O_2]}{k_{15}[M]} \ ,$$

$$k_g\,[RCOOO^{\cdot}]\,[M] = k_{12}\,[M^{\cdot}]\left[\rangle NO^{\cdot}\right] = W_0 \ ,$$

the following equation is obtained:

$$\frac{k_1 k_g [O_2]}{k_7(k_h + k_i)} > \left[\rangle NO^{\cdot}\right] > \frac{k_{14}\,(W_0 k_{15})^{1/2}\,[O_2]}{k_{12}k_{15}\,[M]} \ . \qquad (20)$$

Condition (20) defines the limits of the nitroxy-radical concentration range in which selective inhibition of polymerisation processes, accompanying the oxidation in the acetaldehyde–styrene system, should be observed. The boundary condition for other systems can be derived analogously.

The phenomenon of selective inhibition can be observed in the oxidation of not only binary systems but also of individual compounds having several functional groups with different reactivities, for example, unsaturated aldehydes. This has been used, in particular, in the development of an effective method for the preparation of methacrylic acid[87] by the liquid-phase catalytic oxidation of methacrolein in the presence of the nitroxy-radicals (I) or their 4-hydroxy-derivatives. It is distinguished by simplicity and economy compared with the industrial method of synthesis of methacrolein from acetone via the cyanohydrin. Fig.5 illustrates kinetic curves for the liquid-phase oxidation of methacrolein to methacrylic acid. The use of nitroxy-radicals makes it possible to increase the selectivity in the formation of methacrylic acid to 75–80 mole %. Acetic acid, which also has many applications, is mainly formed as a side product.[97]

In conclusion we shall formulate the necessary and sufficient conditions for selective inhibition:

(1) the existence in the system of two types of free radicals each of which is responsible for the formation of a specific product or group of products; (2) the independence of the concentration of radicals of one type from that of the radicals of the other type; (3) the presence in the system of a definite amount of inhibitor satisfying condition (20); (4) the maintenance of the required inhibitor concentration for a period sufficiently long to ensure the occurrence of a chemical reaction; when nitroxy-radicals are used, this condition is usually fulfilled by means of effective regeneration.

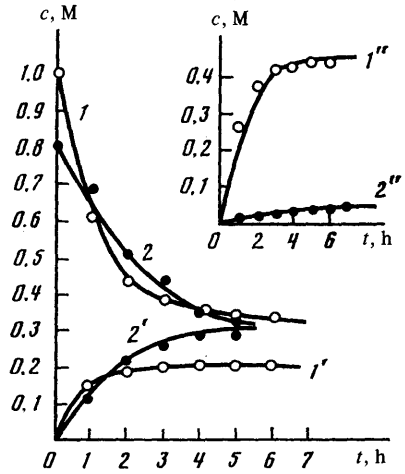


Figure 5. Kinetic curves for the consumption of methacrolein (curves *1* and *2*) and the accumulation of methacrylic acid (curves *1'* and *2'*) and the sums of the side products (curves *1''* and *2''*) in the liquid-phase oxidation of methacrolein by air in benzene (70 °C, 25 atm, 2.5 g litre^{-1} of the TiB_2 catalyst: 1) without inhibitor; 2) in the presence of 1.2×10^{-5} M 4-hydroxy-derivative of the nitroxy-radical (I).[97]

The possibilities in the application of nitroxy-radicals in chemistry are not limited to those already known, the most important of which at the present time are the photostabilisation and inhibition of the oxidative degradation of polymers, the stabilisation of monomers, and also the detection and determination of the active chemical species. Under conditions where the petrochemical raw material resources are diminishing, the ability of nitroxy-radicals to increase the selectivity of the oxidative conversion of hydrocarbons into the required products is very important from both theoretical and practical points of view. The possibility of increasing the efficiency of such processes is associated with the search for new, more effective and at the same time cheap nitroxy-radicals and also with the development of economical methods of synthesis of nitroxy-radicals which are likely to satisfy the future requirements of the chemical industry.

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