A new nuclear spin selective reaction of molecular oxygen

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During high-temperature (623—673 K) oxidation of polyarylenes (polypyromellitimide and polyphenylquinoxaline), the molecular oxygen is enriched in the ^{18}O nonmagnetic isotope and impoverished in the ^{17}O magnetic isotope. The isotope selection increases with the increase in the degree of conversion of oxygen. The spin-selective reaction responsible for the selection of the ^{17}O isotope is the addition of molecular oxygen to triplet exited aromatic fragments of macromolecules to give endoperoxides. This reaction, which is selective in terms of the electron spin, is also nuclear-spin selective resulting in a magnetic isotope effect. The selection of nonmagnetic isotopes, ^{16}O and ^{18}O, is caused by competition between the reversible and irreversible decomposition of endoperoxide and by the classical isotope effect in these reactions.

Key words: magnetic isotope effect, isotope selection, molecular oxygen, oxygen isotopes, oxidation of polyarylenes, polypyromellitimide, polyphenylquinoxaline.

The distribution of isotopes between the products of chemical reactions results from two kinetic isotope effects. The first of them, the well-known classical isotope effect (CIE), is the dependence of the rate of a reaction on the masses of the nuclei of the reacting species; the second, nonclassical magnetic isotope effect (MIE), is the dependence of the rate on the spins and magnetic moments of nuclei. The first effect characterizes the nuclear-mass selectivity of chemical reactions and the second effect determines their nuclear-spin selectivity. Both effects have been experimentally observed for isotopes of oxygen.[1—4] In the chain oxidation of polymers by molecular oxygen, the recovered oxygen was enriched in the ^{17}O and ^{18}O isotopes with respect to ^{16}O and the enrichment in both isotopes increased as the degree of conversion of oxygen in the reaction increased.

Both effects are sensitive to the length of the oxidation chain: the longer the kinetic chain, the lower the isotope selectivity. The enrichment in the ^{17}O isotope is severalfold greater[2,4] than in ^{18}O. Finally, the enrichment in ^{17}O substantially depends on the temperature (its magnitude is maximum in the region of viscoelastic behavior of polymers), whereas for ^{18}O, the enrichment, as might be expected, generally does not depend on the temperature.[2]

It has been inferred that the termination of kinetic chains, *i.e.*, recombination of the $RO_2^{\cdot}$ radicals ($R^{\cdot}$ is an alkyl radical or a macro radical) is a spin-selective and, consequently, a nuclear-selective reaction. It is accompanied by the generation of an unstable intermediate, *viz.* the ROOOOR tetroxide, which decomposes with regeneration of an O_2 molecule from the central oxygen atoms. Contact between peroxide radicals in the singlet spin state is accompanied by their recombination without any substantial spin conversion. The triplet-singlet conversion of triplet pairs of contacting peroxy radicals is induced by the magnetic hyperfine interaction (HFI), which encourages recombination of the peroxy radicals containing ^{17}O magnetic nuclei and, consequently, results in the enrichment of the tetroxide and the molecular oxygen produced from it in the ^{17}O isotope. A similar triplet-singlet conversion depending on the magnetic moment of the nucleus and occurring in biradicals was suggested by Turro[3] as an explanation of the enrichment in ^{17}O of the molecular oxygen formed during thermolysis of endoperoxides.[3]

In the liquid-phase oxidation of ethylbenzene, isopropylbenzene, and solutions of atactic polypropylene, the isotope distribution had the opposite sign:[4] the molecular oxygen was enriched in the ^{18}O isotope and impoverished in the ^{17}O isotope. This behavior was explained by the MIE and CIE in another spin-selective process, *viz.* the reaction of chain growth, $R^{\cdot} + O_2 \rightarrow RO_2$. Owing to the CIE, the oxygen molecules containing ^{18}O are less reactive. On the other hand, molecules with ^{17}O are more active, since the quartet-doublet spin conversion in a $(R^{\cdot}...O_2)$ pair with a full spin of 3/2 is accelerated by the HFI at the ^{17}O atom in the oxygen molecule. Consequently, the CIE in the $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$ reaction induces the enrichment of O_2 in the ^{18}O isotope, whereas the MIE encourages transformation of

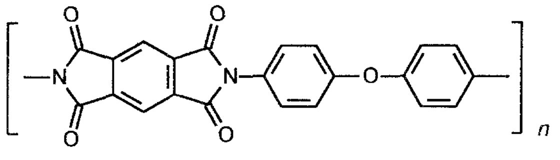
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1402—1405, August, 1994.

molecules with ^{17}O into peroxy radicals and then into hydroperoxide molecules, and hence results in a depletion of the residual molecular oxygen in the ^{17}O isotope.

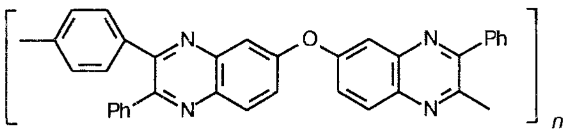
In this paper we describe the behavior of isotopes of oxygen that cannot be assigned to any of the above-described spin-selective reactions, either to the recombination of peroxy radicals or to the addition of oxygen to alkyl radicals.

Experimental

Heat-resistant polyarylenes; polypyromellitimide (PI) with repeating unit of the following structure



and polypnenylquinoxaline (PQ),



were subjected to oxidation by molecular oxygen.

The polymers were prepared by polycondensation of the corresponding monomers. They are poorly soluble in common organic solvents. The high-temperature oxidation of 50 μm thick PI and PQ films was carried out in ampules at an oxygen pressure of 600—700 Torr. After the oxidation, the ampules were opened *in vacuo*, and the amount of the remaining oxygen and the degree of its conversion were determined on the basis of the pressure. Then the oxygen was entirely frozen out onto silica gel and purified by passing it through a filter of porous glass at 77 K 3—4 times. Then the oxygen was frozen onto silica gel into ampules, which were sealed and transferred into a Varian MAT-230 mass spectrometer for isotope analysis. The isotope enrichment was measured as the $S = \delta/\delta_0$ ratio between the $\delta = (^{17}O/^{16}O)$ isotope content in the oxygen after the reaction and $\delta_0 = (^{17}O/^{16}O)_0$ in the starting oxygen. Similar relationships were used for ^{18}O. Coefficient α of the one-stage enrichment is defined by the equation:[6]

$$\log S = (1 - \alpha)\log(1 - F),$$

where F is the degree of conversion of oxygen, $F = [(O_2)_0 - (O_2)]/(O_2)_0$.

Results and Discussion

The changes in the isotope composition of the molecular oxygen summarized in Table 1 exhibit the following regularities:

1) The remaining oxygen is enriched in the ^{18}O nonmagnetic isotope and is impoverished in the ^{17}O magnetic isotope (the nucleus spin is 5/2, the magnetic moment is 1.893 nuclear magnetons). This behavior is at variance with the prediction of the classical isotope effect, according to which both heavy isotopes, ^{17}O and ^{18}O, should be less reactive and should accumulate in the unreacted molecular oxygen.

2) Both effects, the enrichment of the remaining oxygen in ^{18}O and its depletion in ^{17}O, increase, as the degree of oxygen conversion increases.

3) The changes in the isotope composition are identical for both polymers and are generally not dependent on their chemical composition.

The anomalous isotope selection of ^{17}O and ^{18}O forces us to look at spin-selective reactions involving molecular oxygen, which would also be selective with respect to the nuclear spin. As was noted in the introduction, of two such reactions, *viz.* recombination of peroxide radicals and addition of oxygen to alkyl radicals, only the latter results in the $^{17}O/^{18}O$ isotope anomaly. This explanation is only admissible provided that the oxidation is a free-radical chain process. However, its kinetics and the chemical composition of its products are not in line with this condition.

The major products of oxidation are CO (16 %), CO_2 (60 %), H_2O (15 %) (given in parentheses is the relative yield with respect to gaseous products), and quinoid compounds in the solid polymer.[7—9] The rates of formation of gaseous products exactly follow the rate of oxygen absorption. At the initial stages of the process, about 50 % of the oxygen absorbed remains in the

Table 1. The change in the isotope composition $\Delta\delta = (\delta - \delta_0)/\delta_0$ of molecular oxygen, the isotope enrichment S, and coefficients α of the one-step enrichment of the ^{17}O and ^{18}O isotopes

Polymer	T/K	F	$\Delta\delta_{^{17}O}$ (‰)	$\Delta\delta_{^{18}O}$ (‰)	S_{17}	S_{18}	α_{17}	α_{18}
PI	673	0.30	−2.91	+1.56	0.9971	1.0015	0.992	1.004
		0.50	−4.21	+2.21	0.9958	1.0022	0.994	1.003
		0.50	−4.15	+1.03	0.9958	1.0010	0.994	1.0015
		0.65	−6.62	+6.08	0.9934	1.0061	0.994	1.006
PQ	673	0.30	−5.54	+4.22	0.9945	1.0042	0.984	1.012
	623	0.30	−1.68	+0.27	0.9983	1.0003	0.995	1.001
		0.50	−2.73	+4.77	0.9973	1.0048	0.996	1.007

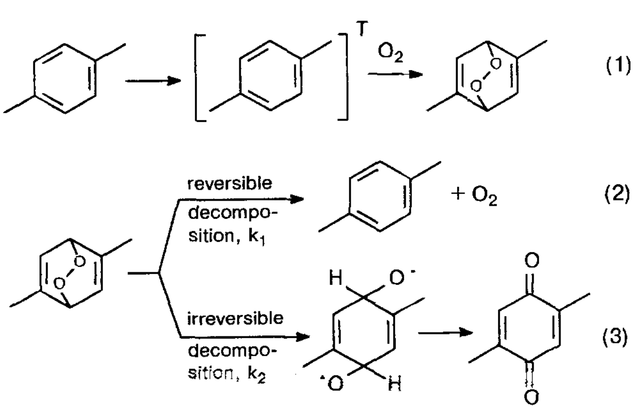
polymer (mainly as the oxygen of carbonyl groups in the quinoid structures and to a small extent in other compounds). The other 50 % of the oxygen goes away in the gaseous products. The chemical nature of the products indicates that the transformation of an oxygen molecule into oxygen-containing products is accompanied by its destruction. This has also been confirmed by experiments[10] on the oxidation of polymers with ^{18}O labelled oxygen: almost all of the CO_2 and 50 % of the H_2O contained the ^{18}O isotope. At the same time, the carbon monoxide contained almost no label, though in the presence of oxygen the rate of its formation increased many times; apparently, CO is formed from fragments of macromolecules during their oxygen-initiated destruction.

One more important feature of the oxidation of polyarylenes is the high degree of crosslinking of the polymers accompanied by the complete loss of their solubility at the initial stages of the oxidation. Both of these effects, *i.e.*, the destruction of the oxygen molecules and the considerable predominance of crosslinking over destruction of the polymer imply that the standard chain radical mechanism of oxidation of polyarylenes is unacceptable. This is also supported by the fact that typical inhibitors of chain radical oxidation are absolutely inefficient in suppressing the oxidation of polyarylenes.

These unusual properties of the oxidation-destruction process cause one to accept an unusual scheme for the oxidation of polyarylenes, which involves the interaction of the low-energy and, hence, thermally accessible, triplet excited states of the aromatic fragments of macromolecules with molecular oxygen to yield endoperoxides (Scheme 1, reaction 1). The latter may decompose according to two channels (reactions 2 and 3).

One of these routes is accompanied by recovery of the aromatic fragment and the oxygen molecule, while the other route results in the formation of quinoid structures.

Scheme 1



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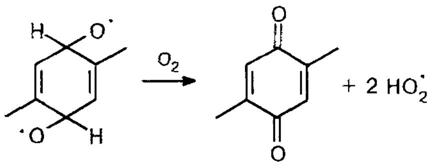
The conversion of the endoperoxide into quinone occurs *via* biradical **1** with alkoxyl-type radical centers. It is known that alkoxyl radicals tend to undergo decomposition reactions (for example, $(CH_3)_3CO^{\cdot} \rightarrow (CH_3)_2CO + CH_3^{\cdot}$) including those with abstraction of a hydrogen atom in the β-position. This means that the conversion of the biradical into the quinoid structure may occur by the same mechanism and involve the abstraction of β-hydrogen atoms. In fact, in the oxidation of polyarylenes, molecular hydrogen (~0.01 mass.%) can be detected; moreover, the rate of its formation is proportional to the rate of oxidation.[11] It is unlikely that any other route for its formation, apart from decomposition of the biradical, will be discovered. The other pathway involves interaction of the biradical with molecular oxygen to give a quinoid structure and $HO_2^{\cdot}$ radicals:



(4)

Notice that the irreversible decomposition of endoperoxides of various structures provides a key to understanding the mechanism of the oxidative destruction of polyarylenes and to the explanation of the composition of the products and kinetic regularities of the process, however, this aspect lies outside the scope of the present paper.

In addition to "chemical arguments", there also exists another factor supporting reaction (1) as the key step of the oxidation of polyarylenes. A measure of the reactivity of aromatic fragments in their transformation to endoperoxide structures is the change in the π-electron energy in this reaction (or the L_π localization energy), which can be calculated, for example, by the Pariser—Parr—Pople method.[12] The higher this energy, the more difficult the transformation of an aromatic structure to an endoperoxide structure. The L_π energies have been calculated for a vast variety of aromatic structures,[13] and it was found that the L_π sequences match sequences of the thermooxidation stability of polyarylenes, their aromatic fragments, and low-molecular-weight compounds simulating one or two repeating units of macromolecules.[13] This correlation cannot be accidental and is an argument for reaction (1).

Finally, the isotope effects (see Table 1) and redistribution of oxygen isotopes observed by us can only be explained by taking into account reaction (1).

The addition of oxygen to the aromatic fragment in the triplet state (T) is preceded by the formation of a $(T...^3O_2)$ pair, whose full spin may be equal to 0, 1, or 2; the corresponding spin states of this pair are singlet, triplet, and quintet. For only one (the singlet) of these nine states $(1+3+5 = 9)$, addition to oxygen to yield the endoperoxide is allowed in terms of the spin. The spin of the other eight states (S = 1 and S = 2) is not equal to that of the product (S = 0) and, consequently, these states are chemically nonreactive. (This conclusion does not depend on whether process (1) occurs as a concerted reaction or *via* the intermediate peroxide biradical.)

However, in the case of pairs containing O_2 with ^{17}O nuclei, the magnetic hyperfine (electron-nuclear) interaction induces a spin conversion of the S = 1 and S = 2 states, forbidden for the reaction, into the S = 0 state, which is allowed for this reaction. Consequently, an additional reaction channel, which selectively impoverishes the molecular oxygen in the ^{17}O magnetic isotope, appears.

Thus, reaction (1), which is selective in terms of the electron spin, becomes as well selective in terms of the nuclear spin (through the electron-nuclear magnetic interaction) and results in the selection of magnetic and nonmagnetic isotopes of oxygen. In other words, reaction (1) is responsible for the spin isotope effect (similarly to the recombination of peroxide radicals and the addition of oxygen to alkyl radicals, see introduction).

Reaction (1), the combination of the two triplet molecules, seems to occur without an activation barrier, therefore it should not involve the classical isotope effect responsible for the separation of the ^{17}O and ^{18}O isotopes in the $^{16}O/^{17}O/^{18}O$ triad (or this effect should be negligibly small). The classical isotope effect originates from the subsequent decomposition of the endoperoxide (reactions (2) and (3)). One may assume that the energy barrier to irreversible decomposition is higher than that for reversible decomposition, and the $^{18}O/^{16}O$ isotope effect should be greater in the case of irreversible decomposition. Then the ratios of the k_1 and k_2 rate constants between the isotope forms with ^{16}O and ^{18}O are expressed as follows:

$$\frac{(k_1)_{18}}{(k_1)_{16}} = \varphi_1 < 1 \quad и \quad \frac{(k_2)_{18}}{(k_2)_{16}} = \varphi_2 < 1 \ ,$$

where $\varphi_2 < \varphi_1$. From this we obtain:

$$\left(\frac{k_1}{k_2}\right)_{18} > \left(\frac{k_1}{k_2}\right)_{16}$$

i.e., the endoperoxides with ^{18}O have a higher probability of undergoing reversible decomposition than those incorporating the "light" isotope, ^{16}O. Consequently, the molecular oxygen recovered is enriched in the ^{18}O "heavy" isotope, while ^{16}O predominantly remains in the quinoid compounds.

Notice that the same classical effect should result in enrichment of the recovered molecular oxygen in the ^{17}O isotope with respect to ^{16}O. However, the magnetic isotope effect (having the opposite sign) for ^{17}O is so significant that it balances out the classical effect or even exceeds it, thus ensuring the depletion of the ^{17}O isotope in the oxygen.

As a generalization of the results of the analysis of isotope selection in the reactions of triplet molecules with molecules of oxygen, it is easy to predict that similar isotope effects should be expected in the oxidation of polynuclear aromatic compounds, graphite, and polyphenylenes both in the photogeneration of triplet states and in the thermal excitation of triplet states, when they lie sufficiently low and are thermally accessible.

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The authors are grateful to E. M. Galimov and I. V. Nikulina for high-quality isotope analyses and to the Russian Foundation for Basic Research for financial support (grant 93-03-5227).

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Received February 8, 1994