Article

Magnetic Field Effect on the Oxidation of Unsaturated Compounds by Molecular Oxygen

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Abstract: A quantum-chemical analysis of the effect of a constant magnetic field on radical formation in the processes of chain oxidation of organic compounds by molecular oxygen is presented. The calculation of the total electronic energies and thermodynamic functions of the compounds involved in the reactions was performed by the density functional method with the hybrid exchange-correlation functional of Becke, Lee, Yang and Parr DFT B3LYP/6-311G** using the NWChem software package. The effect of the magnetic field on the individual stages of chain oxidation is associated with the evolution of radical pairs. It is assumed that the dipole–dipole interaction in a radical pair is not averaged by the diffusion of radicals and should be taken into account. To a large extent, the magnetic field effect (MFE) value is influenced by the ratio between the relaxation time of the oscillatory-excited state in the radical pair (t_{vib}) and the relaxation time of the inter-combination transitions (t_{st}). Although the developed technique refers to liquid-phase reactions, it can be used to study the MFE for oxidation of biologically significant compounds in multiphase systems, such as micelles, liposomes and membranes.

Keywords: magnetic field effect; quantum-chemical analysis; chain oxidation evolution radical pairs; relaxation time inter-combination transitions; relaxation time oscillatory-excited state

1. Introduction

1.1. Background and Motivation of the Research

The magnetic dependence of biosystems usually shows itself at the level of elementary biochemical processes in which spin particles originate or participate. The unpaired electrons in them happen to be spin magnetism carriers; it is these unpaired electrons that interact with magnetic fields [1–9]. The magnetic effect manifests itself in the competition of various channels of transformation in the elementary stages of a reaction and is caused by the dependence of the efficiency of the chemical process on the spin state of a pair of reacting particles (the theory of radical pairs) [2,5,10–15], as well as the magnetosensitivity of transitions between spin states. The effect of stationary magnetic fields on the recombination of radical pairs in molecular oxygen oxidation is one of the well-known mechanisms of interaction of the magnetic field with various biological systems. It can increase the activity, concentration and lifetime of free radicals, which causes oxidative stress, genetic mutation and/or apoptosis [1,2,4,9,10,16]. At the same time, the main role of singlet–triplet transitions in radical pairs is played by Δg, HFC and relaxation mechanisms [2,5,10,14,15,17–23]. A number of studies have revealed the effects of the influence of weak magnetic fields (1 Tl) on individual stages of chain oxidation of unsaturated compounds [10,17–20]. The analysis of these effects can shed some light on the characteristics of the mechanisms of oxidation of biologically significant polyunsaturated fatty acids and their esters, oxidation in micelles, membranes, etc.

1.2. The Basic Mechanism

A theoretical analysis of the effect of a stationary magnetic field (MF) on the detailed mechanisms of radical chain oxidation of organic compounds and experimental data obtained indicates that the stages in generation (initiation), propagation by the reaction of oxygen addition to alkyl radicals and chain termination are magnetically selective [2,8–10,17–20].

A convenient model in such studies can be created from unsaturated compounds of different classes, of which the oxidation mechanism is described by a well-known kinetic Scheme 1 [24,25].
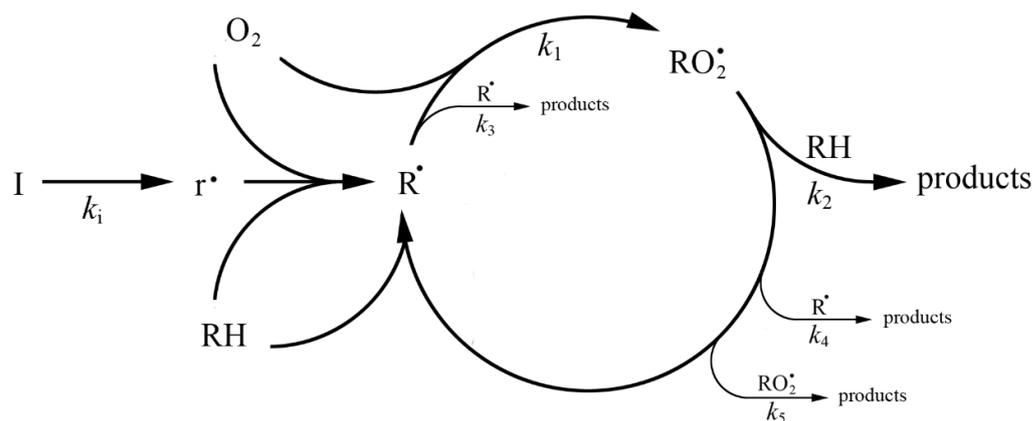
Scheme 1. The mechanism of radical chain oxidation of unsaturated compounds, where I—initiator, RH—unsaturated compound or its saturated analog.

Reaction (2) can also occur as an addition to the π-bond: $RO_2{}^\bullet + CH_2=C< \rightarrow ROOCH_2\text{-}C^\bullet < (\equiv R^\bullet)$, and the primary oxidation product is not hydroperoxide but, rather, peroxide. In accordance with the Scheme 1, the following equation is valid for the oxidation rate (W), where W_i is the chain initiation rate [24]:

$$W = \frac{k_2[\mathrm{RH}]W_i{}^{0.5}}{k_5{}^{0.5}}\left[1 + \frac{k_4}{k_5}\frac{k_2[\mathrm{RH}]}{k_1[\mathrm{O_2}]} + \frac{k_3}{k_5}\left(\frac{k_2[\mathrm{RH}]}{k_1[\mathrm{O_2}]}\right)^2\right]^{-0.5} \tag{1}$$

At moderate temperatures ($\leq 100\ ^\circ C$) and $[\mathrm{O_2}] \leq 0.3$ mM at low transformation depths ($\leq 1\%$), reactions (3) and (4) can be excluded and the oxidation rate (W) obeys the well-known equation [24]:

$$-d[\mathrm{O_2}]/dt = W = k_2 \cdot k_5{}^{-0.5} \cdot [\mathrm{RH}] \cdot W_i{}^0. \tag{2}$$

(if initiation chains are generated by the reaction of molecular oxygen with a substrate molecule ($O_2 + RH$), the value of chain nucleation rate W_0 is used instead of W_i [24,25]).

Obtaining kinetic information about the influence of the magnetic field on each individual stage is experimentally difficult since we deal with a multi-stage radical chain process. Therefore, to find the magnetic field effect (MFE), a methodology of the research of the detailed mechanism of chain oxidation reactions (a detailed description can be found in monographs) [24,25], and a set of experimental and theoretical methods, including quantum calculations and kinetic computer modeling, are used.

Detailed kinetic analyses of the chain propagation and termination reactions were carried out in [10,17–20]. Therefore, the present work is only devoted to the quantum-chemical analysis of the effect of a constant magnetic field on chain oxidation initiation reactions in the reactions of initiator decay and chain generation in the processes of molecular oxygen addition to the π-bond of the oxidized substrate.

2. Methods

The calculation of total electronic energies and thermodynamic functions of the compounds involved in the reactions were performed using the quantum chemical density functional method [26,27] with the hybrid exchange-correlation functional of Bechke [28], Lee, Yang and Parr [29] DFT B3LYP/6-311G** [30] using the NWChem software package [31]. The calculation of Δg-tensors and A-tensors of radicals was carried out using the DFT method in the approximation of a two-component relativistic regular approximation of zero-order (approximate two-component relativistic zeroth-order regular approximation) (ZORA) [32,33], implemented in the NWChem package [34].

In the process of molecular dynamic modeling, the energy and gradient at each step of the integration of the classical equation of motion were calculated using the same DFT B3LYP/6-311G** quantum chemical method. The initial rate of distribution corresponded to the Maxwell–Boltzmann distribution. A thermostat was used to maintain the temperature [35], and the relaxation parameter was equal to 100 integration steps in time.

3. Results and Discussions

3.1. Reactions Chain Initiation of Chain Oxidation

The AIBN was used as an initiator decay by a known mechanism >(CN)CN=NC(CN)<$\rightarrow$ >2(CN)C$^\bullet$ + N$_2$ through the formation of geminal pairs [r$^{\bullet\,\bullet}$r] [2,10,12,13]. During the thermal initiator decay, a radical pair arises under the action of an oscillatory quantum of energy, that is, before the decay, the molecule is in an excited state of oscillation. At the same time, its initial spin state is a singlet.

In the future, depending on the relaxation time of the vibrationally excited state, the pair can recombine by emitting an oscillatory quantum or the radicals can escape into the volume. In this case, the release of radicals into the volume can occur in the initial singlet state or a singlet–triplet conversion can occur in a radical pair [10–14]. Henceforth, depending on the relaxation time of the oscillational excited state, the pair can recombine by emitting an oscillatory quantum, or the radicals can exit into the volume. In this case, the release of radicals into the volume can occur either in the initial singlet state or a singlet–triplet conversion can occur in a radical pair [10–14].

When analyzing the MFE on the initiation reaction, it is necessary to take into account the general laws of the spin dynamics of radical pairs which are also considered in detail in a number of review papers [10–14].

Among all the effects that determine the MFE on the probability of a singlet–triplet transition in a radical pair, we must first distinguish the interaction of unpaired electrons with an external magnetic field, characterized by the g-tensor (the Zeeman effect) and the interaction of electrons with magnetic nuclei of radicals that are characterized by the hyperfine interaction tensor A (the Fermi effect). In qualitative analysis of the MFE on the oxidation kinetics, it is sufficient to compare the orders of these effects for interacting radicals [17–20]. However, for a detailed analysis, a computer modeling of the effects under consideration is necessary since the mismatch of the oscillatory dynamics of radicals in a pair in the pre-emission state can change both their g-tensors and hyperfine interaction tensors, which can affect the probability of singlet–triplet conversion.

In ordinary organic molecules, the excited triplet level has a significantly higher energy than the main singlet and spin-forbidden singlet–triplet transitions are unlikely. At the same time, for initiators with lower bond decay energy, the number of oscillatory levels increases rapidly with increasing temperature and the probability of singlet–triplet transitions should also increase simultaneously. Such effects are observed, for example, during thermo- and photoinitiated radical polymerization [36,37]. In this regard, quantum chemical calculations and molecular dynamic modeling of the processes of radical decay of AIBN in singlet and triplet states were carried out in order to assess the possible influence of oscillatory excited states on the probability of singlet–triplet transitions. The integration of the equations of motion was carried out in accordance with the Verlet algorithm; the integration step in time was 0.2419 fs. In the course of quantum chemical calculations,

cross sections of the potential energy surface were studied along the oscillatory coordinate, which is the distance R between carbon atoms C1 . . . C5 (Figure 1), thus characterizing the distance between the fragments of the radical pair.
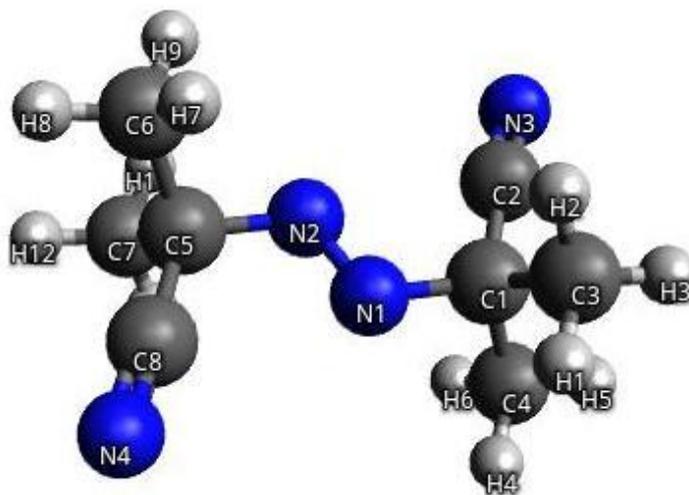

Figure 1. The AIBN structure at the minimum energy.

For this purpose, conditional optimization of the geometry of the system was performed at fixed values of the coordinates of atoms C1 and C5 with different values of *R*. Figure 2 shows the dependence of the difference in the energy of the Δ*E* system in the singlet spin state with respect to the global minimum on the value of *R*.

Molecular structures are shown to be near their local extremes (local maximum and local minimum). It can be seen that dependence can be approximated by a smooth curve. After reaching the maximum, the value of which is about 135 kJ/mol, a local minimum corresponding to the formation of a singlet radical pair is observed. The radical pair structure, with a symmetrical placement of radicals relative to the nitrogen molecule located in the center, corresponds to the concert decay mechanism characteristic of azo initiators [38]. The nitrogen molecule located between the radicals will prevent their recombination in the singlet state and promote the release of radicals into the volume. Figure 3 shows a similar dependence for a system in a triplet state.

The minimum energy of the triplet state lies significantly higher than of the main singlet state, which corresponds to the prohibition of singlet–triplet transitions in the main oscillatory state. However, with the increase in R, the situation changes. When the R value reaches about 0.42 nm, there is a break in the cross section of the potential surface with a sharp drop in the energy value. At the same time, as can be seen from the figure, there is a significant restructuring of the molecular structure with the release of a nitrogen molecule into the volume and the formation of a triplet radical pair. According to the spin prohibition, such a pair should not recombine, and the radicals should also be released into the volume. This conclusion is confirmed by the results of molecular dynamic modeling in the quantum-classical approximation.

Figure 4 shows the time dependences of R in molecular dynamic modeling for AIBN molecules in singlet and triplet states.

For a molecule in a singlet state the R distance does not undergo significant changes, and instead fluctuates relative to the average value corresponding to the minimum potential energy. For a molecule in the triplet state, fluctuations are also initially observed relative to approximately the same value of R; however, after a time of about 250 fs, the distance between the radicals begins to systematically increase, which indicates the decay of the radical pair and the release of radicals into the volume. At this moment a rearrangement of the structure takes place accordant to a break at the intersection of the potential surface (Figure 3). This fact is proved by energy distribution types for the molecule in different spin states obtained in molecular dynamics simulation (Figure 5).

Figure 2. The dependence of the energy changes relative to the global minimum of the AIBN molecule in the singlet state on the distance between carbon atoms C1 and C5 (Figure 1).

At this moment a rearrangement of the structure takes place accordant to a break at the intersection of the potential surface (Figure 3). This fact is proved by energy distribution types for the molecule in different spin states obtained in molecular dynamics simulation (Figure 5).
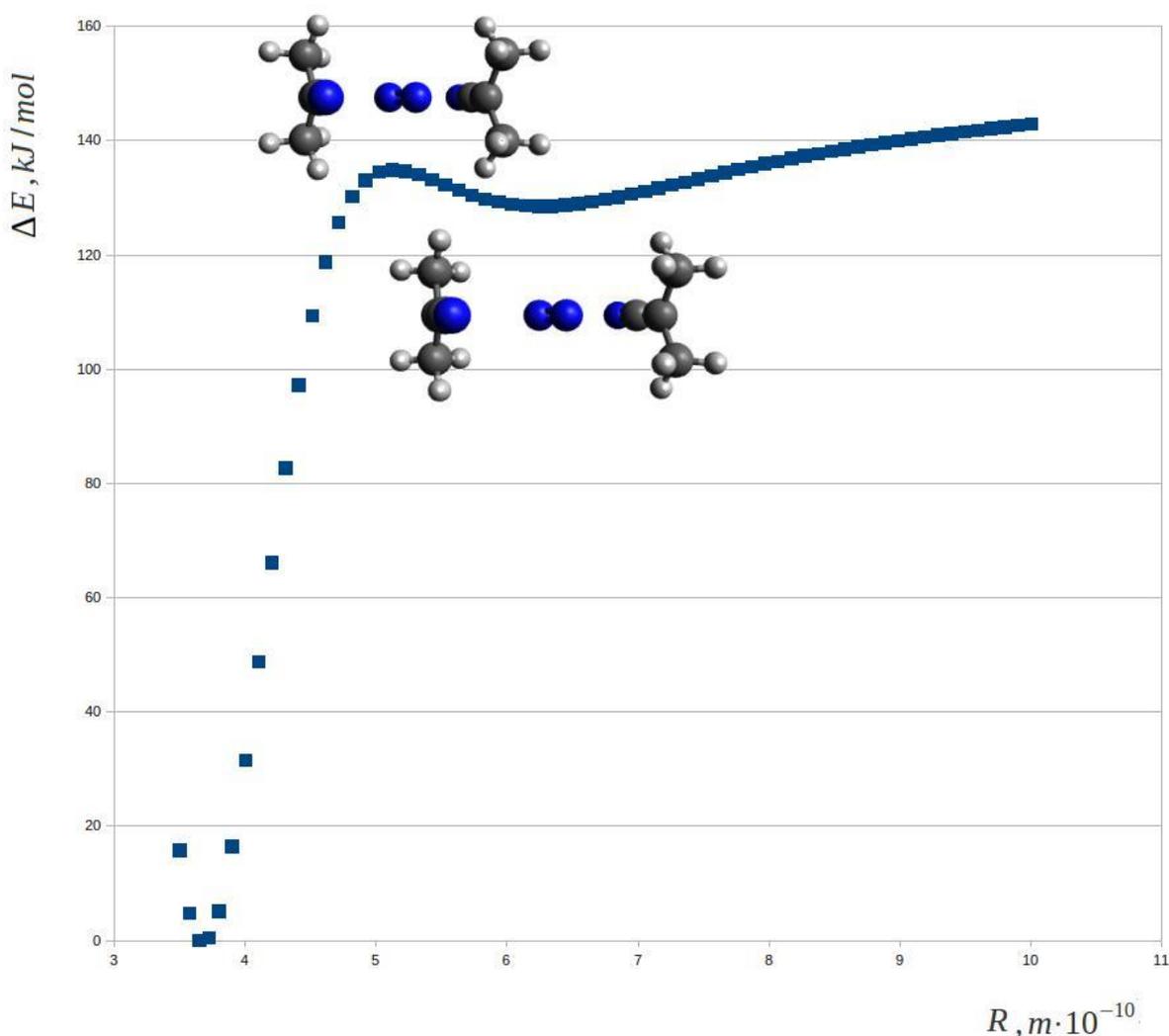
Curve 1 corresponds to the energy distribution of the molecule in the singlet state. Curve 2 corresponds to the distribution of the molecule in the triplet state at simulation time up to 250 fs. Curve 3 corresponds to the distribution of the molecule in the triplet state at simulation time after 250 fs. There are characteristic symmetric distributions for all three curves; however, for a molecule in a triplet state, the dispersion of distributions is slightly higher. It can be seen that curves 2 and 3 correspond to different states. A sharp decrease in energy after 250 fs for the triplet molecule corresponds to a gap in the section of the potential surface in Figure 3 with the exit of the nitrogen molecule from the radical pair. At the same time, as expected, the triplet radical pair is not stable, and the radicals leave into volume. The time required for the relaxation transition from state 2 to state 3 can be characterized as the relaxation time of the oscillatory-excited state—t_{vib}.

The question of whether singlet–triplet transitions occur during the decay of the initiator, and accordingly, whether an external magnetic field will affect the probability of decay, is not obvious. Triplet–singlet transitions are observed during the photoinduced decay of initiators [36,37], while an external magnetic field can have a significant effect. That is, the lifetime of triplet radical pairs is sufficient for an inter-combination transition,

but a singlet radical pair must recombine quickly. An analysis of the decomposition products of azo initiators suggests that such transitions do take place. Particularly in the case of the thermally initiated decomposition, all geminal radical pairs in the absence of inter-combination transitions should be singlets; however, the yield of the recombination products of geminal radical pairs seems to be underestimated, given the significant cellular effect [24,38].
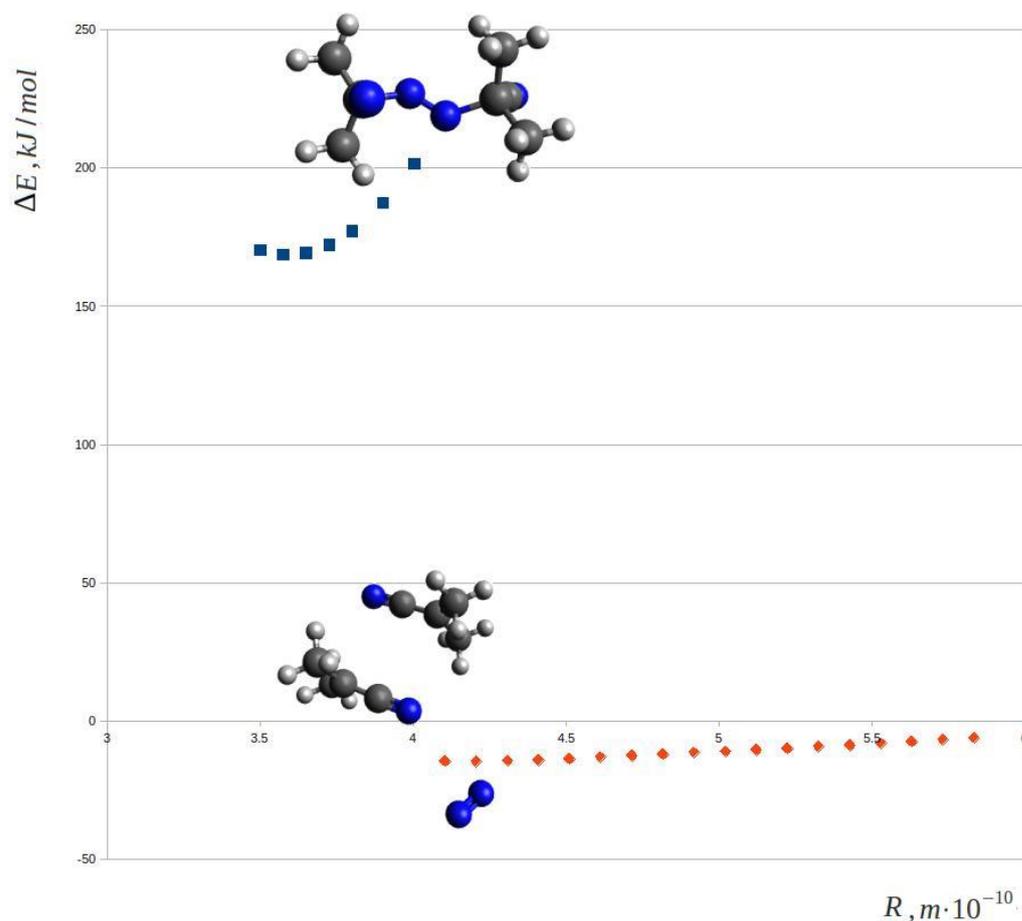

Figure 3. The dependence of the energy change relative to the global minimum of the AIBN molecule in the triplet state on the distance between carbon atoms C1 and C5 (Figure 1).

On the one hand, the identical structure of the radicals in the AIBN decomposition products, which results in the equality of their g-factors in the main oscillatory state, should lead to the absence of the influence of the magnetic field on the probability of conversion by the Δg mechanism. On the other hand, when the process occurs via the cleavage of two bonds with the formation of two radicals and a nitrogen molecule, as in the singlet radical pair in Figure 2, the correlation between the formed radicals will be weakened so that they can be at different oscillatory levels with different values of the oscillatory excited state time (t_{st}). In this case, their g- and A-tensors will differ, which will contribute to the inter-combination transition. In order to evaluate this effect, g- and A-tensors of the $(CH_3)_2C \cdot (CN)$ radicals of singlet and triplet AIBN molecules were calculated at the minimum energy and after 1000 fs of molecular dynamic modeling, which is when the correlation between them is practically absent, and their configurations are very likely to correspond to different oscillating levels. The Table 1 shows the eigenvalues of g-tensors calculated at these times, and as an invariant of A-tensors, the A_{eff} values calculated by the formula [29] are given

$$A_{eff} = \left(\sum AA^T \right)^{\frac{1}{2}} \tag{3}$$

where the *A* symbol denotes the A-tensor in diagonal form, and summation is performed over all the protons of the radical.
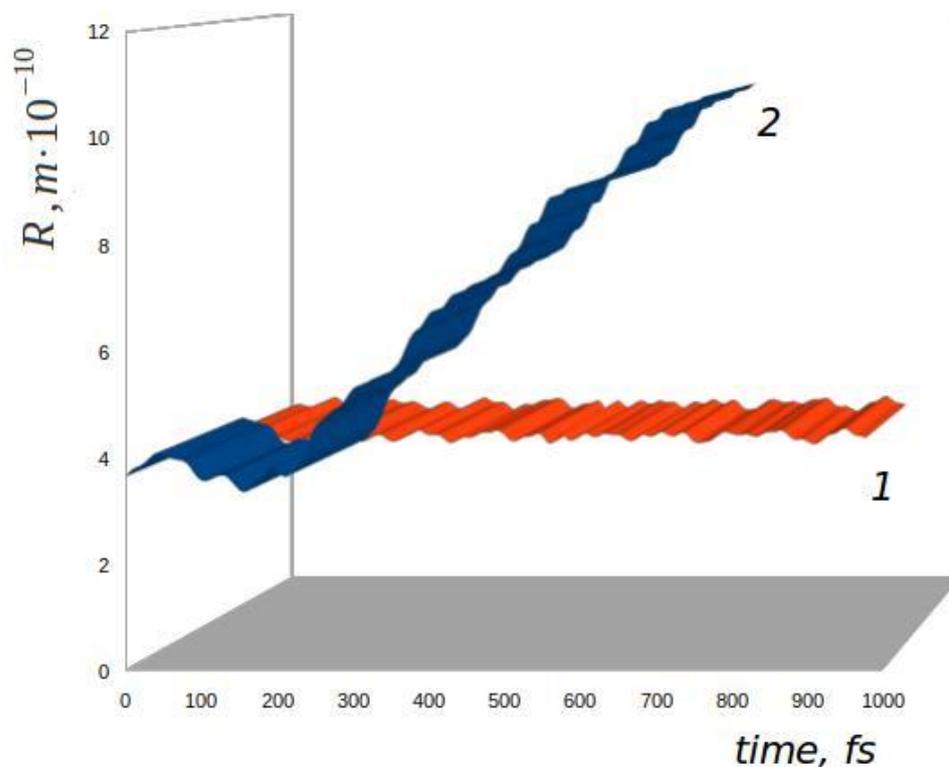

Figure 4. The dependence of the distance between C1 and C5 atoms on the time of molecular dynamic modeling: 1—a molecule in a singlet state, 2—in a triplet state.
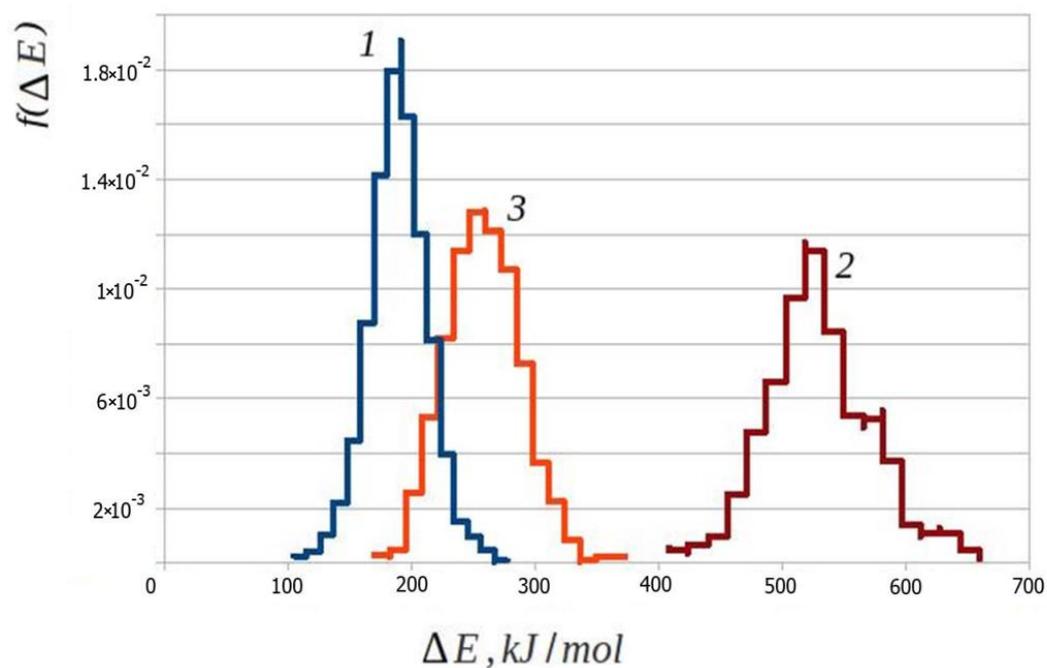

Figure 5. The energy distributions of the AIBN molecule in molecular dynamic modeling: 1—in the singlet state, 2—in the triplet state before the time of 250 fs, 3—in the triplet state after the simulation time of 250 fs.

Table 1. C·(CN) radicals of singlet and triplet AIBN molecules at minimum energy and after 1000 fs of molecular dynamic modeling.

Parameter	$t = 0$	$t = 1$ ps	
		Singlet	Triplet
g_{xx}	2.002226	2.002388	2.002331
g_{yy}	2.003132	2.003412	2.003585
g_{zz}	2.003851	2.004030	2.003647
$A_{eff} \cdot 10^{-8}$, Hz	2.39	1.84	2.80

From the above data, the eigenvalues of the radical g-tensors change during the simulation for both singlet and triplet radical pairs. Although these changes are not very significant, but taking into account the fact that, as can be seen from Figure 5, the energy distributions of the singlet (curve 1) and triplet states (curve 3) do intersect, at certain times the singlet-triplet transition may turn out to be favorable, so such transitions can occur in a strong magnetic field.
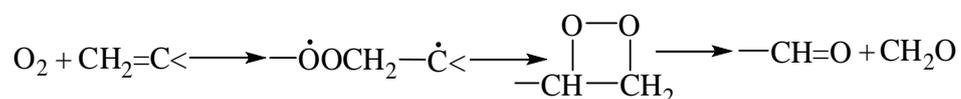
The A_{eff} values indicate that, in strong magnetic fields (MF), S-T_0 inter-combination transitions are also possible via the mechanism of hyperfine interaction with characteristic relaxation times t_{st}.

Thus, the calculation performed indicates the possible effect of an external constant (MF) on the kinetics of the release of radicals into the volume during the AIBN thermal decomposition, which in turn should lead to an increase in the rate of oxidation initiation; this corresponds to the observed experimental data [19]. The degree of influence of an external MF on the rate of initiation will obviously depend in each specific case on the ratio of the relaxation times t_{vib} and t_{st}.

3.2. Chain Generation by Reaction with Dioxygen

Let us consider the reaction of oxygen addition to a double bond in the example of styrene. Here, as in the previous case, the MFE mechanism is realized through the influence of a magnetic field on the probability of a triplet–singlet conversion of a radical pair during the reaction.

In [17,19], based on the experimental data obtained, it was shown that the effect of MF is determined by the mechanism of interaction of O_2 with the π-bond. The reaction proceeds through the formation of a triplet biradical, which initiates oxidation chains: $O_2 + CH_2=C< \rightarrow O_2 + C=C \rightarrow [^{\bullet}OOC-C^{\bullet}]^T \rightarrow {}^{\bullet}OOCH_2\text{-}C^{\bullet}<$ via reactions with O_2 and π-bonds. The Zeeman interaction stimulates triplet–singlet conversion through the T–S transition leading to the formation of non-radical compounds of molecular products (dioxetane and its decay products [24,38]):

$$O_2 + CH_2=C< \longrightarrow -\dot{O}OCH_2-\dot{C}< \longrightarrow \begin{array}{c} O-O \\ | \quad | \\ -CH-CH_2 \end{array} \longrightarrow -CH=O + CH_2O$$

As a result, the share of radical initiation decreases, and the sign of MFE will be negative [19]. At the same time, not all details of this mechanism have been described due to the lack of appropriate quantum chemical calculations.

In the previous case, the magnetic field leads to an increase in S–T transitions; then, the opposite picture takes place in the nucleation reaction: the magnetic field changes the probability of T–S transitions. Since the stable spin state of molecular oxygen is a triplet, the pre-reaction complex, including styrene and oxygen molecules bound by intermolecular interaction, is also a triplet. As a result of the reaction, primary radical pairs may arise, which are also in the triplet state. When unpaired electrons of radical pairs are attached to olefin double bonds, a chain oxidation process begins. At the same time, as a result of triplet–singlet transitions, molecular compounds can be formed in radical pairs. Since in

this case, unlike with the azo initiator initiations, singlet states are lower in energy than the initial triplet, such processes will remove the resulting compounds from the chain process and the MFE sign will be negative. Figure 6 shows the calculated variants of the structures of compounds in the minimum potential energy, reflecting the various stages of formation and evolution of radical pairs that occur when oxygen is attached to the double bond of a styrene molecule.
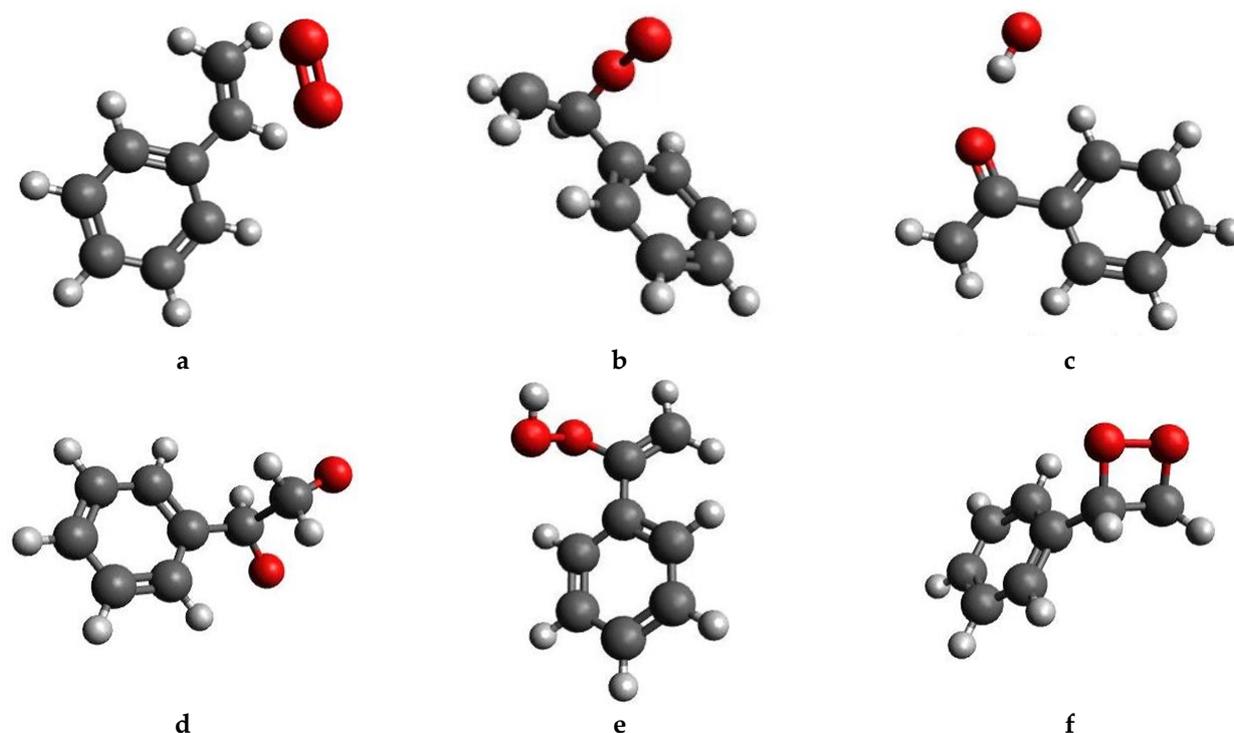
a

b

c

d

e

f

Figure 6. Structures emerging during the reaction of formation and evolution of radical pairs during auto initiation of styrene oxidation: **a**—IT, $\Delta E = -20.8$ kJ/mol; **b**—IIT, $\Delta E = 74.6$ kJ/mol; **c**—IIT, $\Delta E = -33.0$ kJ/mol; **d**—IVT, $\Delta E = 289.5$ kJ/mol; **e**—IS, $\Delta E = -80.9$ kJ/mol; **f**—IIS, $\Delta E = -46.3$ kJ/mol.

For each structure, the values of the change in its energy (ΔE) with respect to the sum of the total electronic energies of isolated styrene and oxygen molecules are indicated. The T symbol at the Roman numeral corresponding to the structure number indicates a triplet state; the S symbol is a singlet state. The IT structure is an initial pre-reaction complex. Structure III is an internal radical pair that occurs when a diatomic oxygen molecule is attached to one of the carbon bonds of a styrene molecule. The IVT structure is a radical pair that occurs when an oxygen molecule is attached to a styrene double bond by two atoms simultaneously. In [19], it was assumed that the IVT structure emerges during the transformation of the IIT structure. However, as can be seen from the energy changes values, this process is unlikely and the process leading to the IIIT structure is more likely. Both radical pairs IVT and IIIT can initiate two kinetic oxidation chains; however, the difference between them is that in the case of the IVT structure, these kinetic chains will start on the same molecule, whereas in the case of the IIIT structure, they will start on two different molecules. The second molecule initiating the chain, in this case, will be a hydroxyl radical. When a constant magnetic field is applied, T–S transitions will be initiated, which in this reaction can be both $T_+ \rightarrow S$ and $T_- \rightarrow S$ depending on the magnetic field strength, and with increasing field strength, the proportion of $T_- \rightarrow S$ transitions should decrease. Since these transitions will lead to the formation of molecular compounds, the share of radical pairs involved in the initiation of oxidation chains will decrease and the MFE sign will be negative.

The reagents evolution scheme in the studied initiation process is shown in Figure 7.
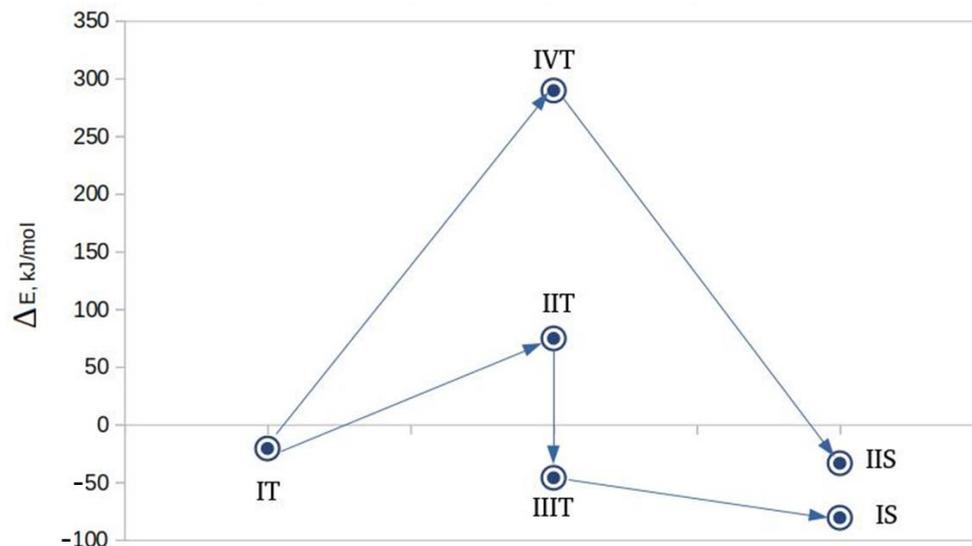

Figure 7. Scheme of the evolution of radical pairs during auto initiation of styrene oxidation.

Since, for all possible types of radical pairs, the final singlet states of the reaction products are lower in energy than triplet ones, the course of these reactions will lead to a decrease in the share of the chain oxidation mechanism as well as to the rate of the entire oxidation process (Figure 7).

4. Conclusions

It can be concluded that the influence of the magnetic field on individual stages of chain oxidation is associated with the evolution of radical pairs. The detected effects may be due to the kinetic features of the detailed mechanism of the chain process. The answer to this question should be sought in a combination of theoretical analysis with experimental study of elementary reactions. The calculations presented in this paper suggest a strong dependence of the MFE on the dipole–dipole interaction in the radical pair. This interaction is not averaged by the diffusion of radicals and must be taken into account. To a large extent, the MFE value is influenced by the ratio of the relaxation time of the oscillatory-excited state in the radical pair, t_{vib}, and the relaxation time of the inter-combination transitions, t_{st}. Although the developed technique refers to liquid-phase reactions, it can nevertheless be used to study the MFE for the oxidation of biologically significant compounds in multiphase systems, such as micelles, liposomes and membranes.

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