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Mendeleev Commun., 2020, **30**, 433–435

Mendeleev Communications

Magnetic field as a means to identify initiating reaction in oxidation of organic substances with molecular oxygen

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DOI: 10.1016/j.mencom.2020.07.009

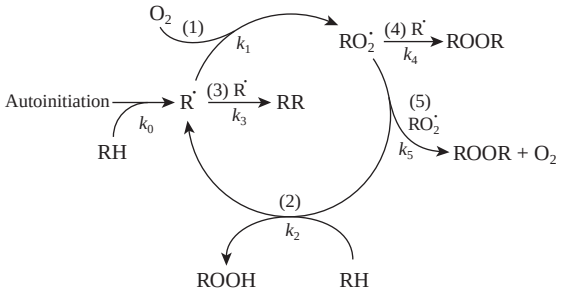
Oxidation of olefins is initiated by addition of oxygen at the π-bond with formation of triplet biradical; therefore, dioxetane formation becomes dominant due to the Zeeman interaction stimulating triplet–singlet conversion through the T–S transition, with the contribution of the radical initiation being lower. In the case of saturated compounds, the Zeeman interaction results in the absence of the magnetic field effect on the rate of radical formation since the chain initiation is ruled by the hydrogen atom abstraction.

$$O_2 + RH \longrightarrow [R^{\bullet} \cdot O_2H]^T$$

$$O_2 + C{=}C \longrightarrow [^{\bullet}OOC{-}C^{\bullet}]^T$$

Keywords: magnetic field effect, chain oxidation mechanism, hydrogen atom abstraction, oxygen, triplet biradical, Zeeman interaction.

The process of oxidation and rotting of organic substances (wood, plants, coal, polymers, micro- and macro-organisms, contaminating oil films and spots on the water of seas and lakes, *etc.*) with molecular oxygen is a global one. It generates in the environment such pollutants as aldehydes, ketones, hydrogen peroxide and organic acids. Biological effects of oxidation related to oxidative stress, mutations and apoptosis[1–7] are also important. It is known that at low conversions the chain oxidation mechanism is described[1] as outlined in Scheme 1.



Scheme 1 The reaction numbering is related to the *k* indices.

The reaction of type (2) can also comprise an addition at the π-bond, namely, $RO_2^{\bullet} + H_2C{=}C\langle \longrightarrow ROOCH_2{-}C\langle(\equiv R^{\bullet})$; as a result, the primary oxidation product is not hydroperoxide but peroxide.[1] In accordance with the scheme for the oxidation rate (W), the following equation can be valid (W_0 is the chain initiation rate):

$$W = \frac{k_2[\mathrm{RH}]W_0^{0.5}}{k_5^{0.5}}\left[1 + \frac{k_4}{k_5}\frac{k_2[\mathrm{RH}]}{k_1[\mathrm{O_2}]} + \frac{k_3}{k_5}\left(\frac{k_2[\mathrm{RH}]}{k_1[\mathrm{O_2}]}\right)^2\right]^{-0.5},$$

which at $[O_2] > 0.3$ mM is converted to $W = k_2k_5^{-0.5}[\mathrm{RH}]W_0^{0.5}$.

In our previous works,[8,9] we have shown that chain propagation (1) and chain termination (3)–(5) stages (see Scheme 1) are magnetically controlled. However, the most important key step is the initiation, therefore, to identify its mechanism we have studied magnetic field effect (MFE) on the oxidation inhibited by radical scavengers (nitroxyl radicals) which would prevent chain reactions leaving oxygen consumption only in the initiating steps.

The list of unsaturated compounds and their saturated analogues is given in Table 1; all substrates were tested as the chlorobenzene solutions in concentration of 50 vol%.†

Table 1 The rates of initiation W_0 and MFE as a function of MF.[a]

Substrate	$W_0 \times 10^8$/mol dm^{-3} s^{-1}		MFE
	MF = 0 T	MF = 0.6 T	
Ethylbenzene, $PhCH_2Me$	0.94	0.96	1.0
Cumene, $PhCHMe_2$	0.87	0.86	1.0
Isobutyl propionate, $MeCH_2C(O)OCH_2CHMe_2$	0.44	0.45	1.0
Styrene, $PhCH{=}CH_2$	5.11	8.72	1.7
α-Methylstyrene, $PhC(Me){=}CH_2$	5.92	9.47	1.6
Butyl methacrylate, $CH_2{=}C(Me)C(O)O(CH_2)_3Me$	13.02	23.45	1.8

[a] Conditions: $[O_2] = 0.3$ mM and $[NO^{\bullet}] = 1 \times 10^{-5}$ M, $T = 353$ K.

† The compounds were purchased from Aldrich, their purity was controlled by HPLC (Flexar, PerkinElmer, USA) and by GC/MS (Clarus 680T MS, PerkinElmer, USA). The initial concentration of peroxides was negligible (less than 1×10^{-6} M) and was controlled electrochemically (potentiometer P-45X) and by iodine titration. The kinetics of oxygen consumption was monitored by measuring oxygen volume at constant oxygen pressure; oxygen concentration was varied in the range 0.3−7.8 mM using mixtures O_2 + Ar. The oxidation was inhibited by addition of stable bis(4-methoxyphenyl)nitroxyl radical; the magnitude of magnetic field (MF) in the reactor was varied in the range 0.2−0.6 T. The concentration of the nitroxyls was monitored by ESR. Magnetic field effect (MFE) was determined as the ratio $W_0(0)/W_0(H)$, where $W_0(0)$ and $W_0(H)$ were the rates of initiation in zero magnetic field and in the field H, respectively. The details of experimental technique and description of the reactor are described in refs. 10–12.

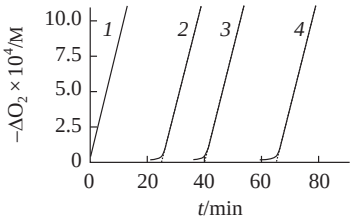


Figure 1 Oxygen consumption in the course of oxidation of styrene inhibited by nitroxyl radicals at concentrations of (*1*) 0, (*2*) 3.1, (*3*) 5.0 and (*4*) 8.0×10^{-5} M.

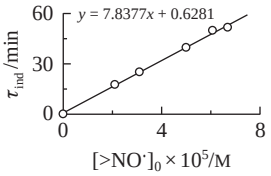


Figure 2 The induction period τ_{ind} as a function of concentration of nitroxyl radicals in the oxidation of α-methylstyrene.

Figure 1 demonstrates that the inhibitor completely retards oxidation which can start only after removal of the inhibitor. The induction period τ_{ind} is linearly dependent on the concentration of inhibitor (Figure 2). The rates of initiation for different substrates are summarized in Table 1 as MFE values.

The most impressive result is that there is no MFE for the saturated substrates (see Table 1), while the unsaturated molecules exhibit MFE of 1.6–1.8 when high fields $H \geqslant 0.4$ T are applied (typical example is shown in Figure 3).

The difference in the MFE value for saturated and unsaturated compounds is caused by different mechanisms of the initial stages. For the saturated ones (Scheme 2), it comprises the hydrogen atom abstraction, which generates radical pair $[R^{\cdot}\ {}^{\cdot}O_2H]^T$ **1** in triplet spin state.

$$O_2 + RH \longrightarrow [R^{\cdot}\ {}^{\cdot}O_2H]^T \quad \mathbf{1}$$

Scheme 2

As for unsaturated substrates, the insertion of oxygen molecule into the double bond is supposed to be the dominating reaction which generates biradical $[^{\cdot}OOC{-}C^{\cdot}]^T$ in triplet spin state (Scheme 3). By definition, the rate of initiation is the radical release from the primary pair **1** or biradical **2**; it competes with intra-cage reactions which are the source of MFE.

$$O_2 + C{=}C \longrightarrow [^{\cdot}OOC{-}C^{\cdot}]^T \quad \mathbf{2}$$

Scheme 3

In the pair **1**, the two reactions may occur, namely, recombination and disproportionation (Scheme 4). The first reaction is spin forbidden and needs spin conversion from triplet state T into the singlet S. Spin conversion is induced by difference in the Zeeman energies $\Delta g\beta H$, where Δg is the difference of *g*-factors of partners; so that magnetic field accelerates recombination decreasing the rate of initiation. On the contrary, the second reaction is spin allowed because it regenerates triplet oxygen; magnetic field stimulates spin conversion from triplet state T into the singlet S with the rate

$$[R^{\cdot}\ {}^{\cdot}O_2H]^T \xrightarrow[H]{T \rightarrow S} [R^{\cdot}\ {}^{\cdot}O_2H]^{SH} \longrightarrow ROOH$$

$$[R^{\cdot}\ {}^{\cdot}O_2H]^T \xrightarrow[H]{T \rightarrow S} [R^{\cdot}\ {}^{\cdot}O_2H]^{SH} \not\longrightarrow O_2 + RH$$

Scheme 4

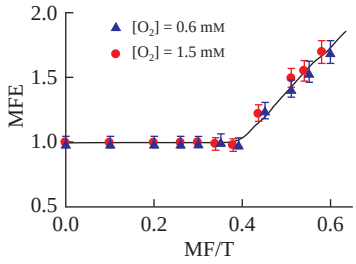


Figure 3 Magnetic field effect on the rate of initiation in oxidation of butyl methacrylate as a function of magnetic field. T = 353 K.

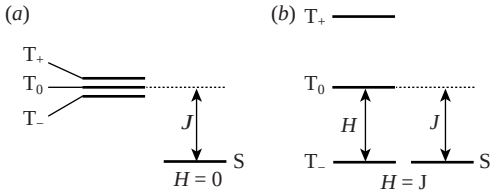


Figure 4 The Zeeman levels in biradical **2** in (*a*) zero magnetic field and (*b*) magnetic field $H \approx J$; H and J are implied here in the energy units.

$\Delta g\beta H$ preventing disproportionation and increasing radical escape, *i.e.* increasing the rate of initiation. Evidently, spin conversions in both reactions occur in the opposite directions and compensate each other. Finally, it results in the absence of MFE on the rate of initiation, in agreement with experimental observations (see Table 1).

In the initially formed biradical $[^{\cdot}OOC{-}C^{\cdot}]^T$ **2**, magnetic field stimulates its triplet–singlet conversion so biradical **2** in singlet state collapses into the peroxide molecule (Scheme 5).

$$-CH{=}CH_2 + O_2 \longrightarrow \underset{-CH-CH_2}{\overset{O-O}{|\quad|}} \longrightarrow -CH{=}O + CH_2O$$

Scheme 5

Magnetic effect starts at high field $H \approx 0.4$ T (4000 G) which is much greater than any hyperfine coupling with protons in biradical **2**; it means that the exchange interaction J in biradical is high. Triplet–singlet conversion occurs as the T_−S transition when T_ state approaches to the S state (Figure 4). It is switched on by spin relaxation, the latter is induced by exchange interaction J modulated by intra-molecular motion in the biradical. The MFE achieves maximum when the positions of T_ and S states coincide (see Figure 4).

The results show that the MFE sorts the routes of oxidation chain initiation reactions. For unsaturated compounds, when this process is carried out by the mechanism of attaching oxygen to the π-bond to form a triplet biradical $^{\cdot}OOCH_2{-}C\overset{\cdot}{<}$, the Zeeman interaction, which stimulates triplet–singlet conversion through the T–S transition, makes the dioxetane formation route dominant, reducing the contribution of radical initiation. For their saturated analogues, when initiation is carried out by the mechanism of the hydrogen atom abstraction: $RH + O_2 \rightarrow HO_2^{\cdot} + R^{\cdot}$, the Zeeman interaction leads to the absence of MF influence on the radical formation.

This research was performed with the financial support of P. G. Demidov Yaroslavl State University (grant no. AAAA- A19-119111290038-4).

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Received: 26th February 2020; Com. 20/6142