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Mendeleev Commun., 2017, **27**, 246–247

Mendeleev Communications

Magnetic field effect on the oxidation of hydrocarbons by molecular oxygen

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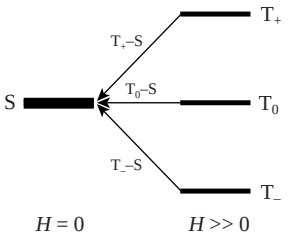
DOI: 10.1016/j.mencom.2017.05.009

Magnetic fields (0.3–0.4 T) were found to accelerate the oxidation of styrene and ethylbenzene with molecular oxygen by 10–70% with increasing the rate of initiation and decreasing the rate of chain termination. The effects are consistently explained in terms of triplet–singlet spin conversion in radical pairs, and they can be used to elucidate the oxidation mechanisms of biologically important molecules (polyunsaturated acids and lipids).



It is a common place that oxidation processes are important both in industry and in nature. Among different oxidation mechanisms, a chain mechanism, which includes radicals as spin carriers, is most general and important; therefore, it implies spin-selective and magnetosensitive steps. The first case when both magnetic field and nuclear magnetic ^{17}O effects were detected was the photooxidation of water by molecular oxygen;[1] this process is of global importance for the monitoring of oxygen turnover in nature. The oxidation of hydrocarbons by molecular oxygen, in which chain carriers are alkyl R and peroxy RO_2 radicals, also contributes to the oxygen turnover. To elucidate the spin selectivity of the process, we studied the influence of static magnetic fields on the oxidation of ethylbenzene and styrene.

The aim of the study was to detect the effects of magnetic fields and to estimate their magnitudes in order to use these effects as a means of discriminating radical mechanisms from nonradical ones, which may operate in the oxidation of biologically important substances.

Oxidation kinetics was monitored by measuring oxygen consumption using a capillary micro volume metric system.[2,†] Figure 1 shows the *M* magnitudes[‡] for the oxidation of styrene initiated by the diazo compound in a field of 0.4 T. Note that the *M* values strongly depend on the oxygen pressure: they are markedly higher at a low pressure (see *1*, Figure 1).

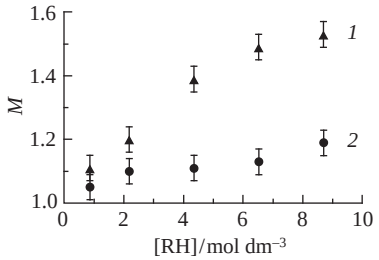


Figure 1 Magnetic field effect *M* as a function of the styrene concentration [RH]. Oxygen pressures, (*1*) 8 and (*2*) 20 kPa; magnetic field, 0.4 T.

Figure 2 demonstrates *M* as a function of [RH] for the autooxidation of styrene. In contrast to the initiated oxidation, in this case, there is no dependence on the oxygen pressure; at least, it does not exceed the limits of errors. The temperature dependence of *M* is also negligible and lies in the same limits. The *M* magnitudes in a field of 0.29 T are smaller, and they do not exceed 1.05–1.12 (not shown in Figure 2).

The initiated oxidation of ethylbenzene exhibits almost similar effects (Figure 3); like in the case of styrene, *M* is significant at low oxygen pressure (8 kPa), but it is lower at 20 kPa (1.06–1.14, not shown in Figure 3).

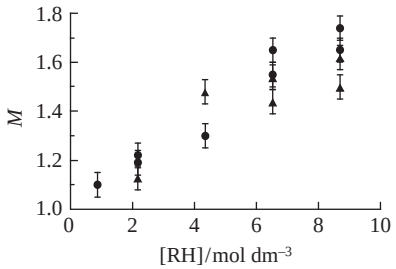


Figure 2 Magnetic field effect *M* as a function of styrene concentration [RH]. Oxygen pressures, (▲) 8 and (●) 20 kPa. Different points refer to temperatures of 60 and 70 °C. Magnetic field, 0.4 T.

† The reaction vessel was immersed in a thermostatic bath supplied with a pair of neodymium magnets (80 × 40 × 20 mm), which produce magnetic fields in a range of 0.2–0.4 T as a function of distance between them. The oxidation was carried out in the solutions of styrene and ethylbenzene in chlorobenzene; azobisisobutyronitrile (AIBN) was used as an initiator. The reactants were purchased from Sigma and purified by chromatography; AIBN was subjected to triple recrystallization. The oxygen partial pressure was varied by mixing with argon; the temperature was varied in a range of 20–80 °C.

‡ Magnetic field effect is defined as the ratio of the oxidation rate in magnetic field $w(H)$ to that in the natural earth magnetic field $w(0)$: $M = w(H)/w(0)$.

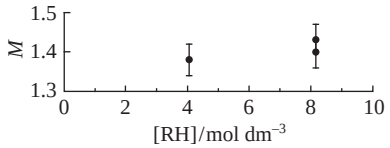


Figure 3 Magnetic field effect on *M* as a function of ethylbenzene concentration [RH]. Oxygen pressure, 8 kPa; magnetic field, 0.4 T.

The chain oxidation by molecular oxygen is known[3–5] to occur as a sequence of initiation, propagation and termination steps:

$$I \rightarrow r^{\bullet}$$
$$r^{\bullet} + RH \rightarrow R^{\bullet} + rH$$
$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$
$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$
$$R^{\bullet} + R^{\bullet} \rightarrow RR$$
$$R^{\bullet} + RO_2^{\bullet} \rightarrow ROOR$$
$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow ROOR + O_2$$

Here, I and RH refer to the initiator and hydrocarbon, respectively; $r^{\bullet}$ and $R^{\bullet}$ are radicals from I and RH, respectively. Only two steps in this scheme are supposed to be spin-selective and hence magneto-sensitive; these are initiation and termination. The above kinetic scheme remains valid for styrene oxidation with the only exception that chain propagation occurs by the addition of a peroxy radical to the double bond of styrene rather than by hydrogen abstraction.

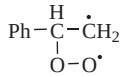
The termination step of initiated oxidation implies recombination and cross-recombination of radicals $R^{\bullet}$ and $RO_2^{\bullet}$. These events occur in the encounters of freely diffusing radicals. In the pairs of encountering radicals, electron spins are uncorrelated; *i.e.*, spin states are random and composed of singlets and triplets with the statistics 1 : 3. Singlet pairs are short living; they fast recombine so that their spin conversion and magnetic field effect in these pairs may be neglected. The alkyl radical recombination $R^{\bullet} + R^{\bullet} \rightarrow RR$ may be certainly ignored at a commonly used oxygen pressure due to the fast reaction $R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$. The recombination $RO_2^{\bullet} + RO_2^{\bullet}$ does not depend on the magnetic field because, in the pair of these radicals both in singlet and triplet states, neither Zeeman interaction nor Fermi (hyperfine) coupling are functioning (both $\Delta g\beta H$ and hyperfine coupling constants a are zero or negligibly small).[6,7]

In the pair $[R^{\bullet}\ {}^{\bullet}O_2R]$, both Zeeman and hyperfine interactions are functioning. In zero or very low fields, hyperfine coupling with the protons of radical $R^{\bullet}$ ($a \approx 20$–25 G) induces the three transitions T_0–S, T_+–S, and T_-–S, each with a rate of about 10^8 Hz. In a high field when $H >> a$ (particularly, in the field $H = 0.4$ T), the two transitions (T_+–S and T_-–S) are switched off; only the T_0–S channel remains. However, Zeeman interaction in the pair $[R^{\bullet}\ {}^{\bullet}O_2R]$ additionally stimulates the T_0–S transition with the rate $\Delta g\beta H \approx 10^8$ Hz, where Δg is the difference of g-factors $g(RO_2) - g(R) \approx 10^{-2}$. Ultimately, a magnetic field switches off two triplet–singlet conversion channels, but it switches on one channel. It decreases recombination probability of the radical pair $[R^{\bullet}\ {}^{\bullet}O_2R]$ and, consequently, increases the oxidation rate, resulting in $M > 1$.

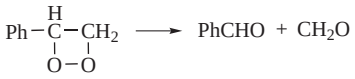
This conclusion is in accordance with experimental data (Figure 1). Moreover, it predicts the dependence of M on the oxygen pressure. The radical pairs $[R^{\bullet}\ {}^{\bullet}O_2R]$ may contribute to chain termination at a low oxygen concentration, but their contribution strongly decreases by the replacement of the pairs $[R^{\bullet}\ {}^{\bullet}R]$ by the pairs $[R^{\bullet}\ {}^{\bullet}O_2R]$, when the oxygen concentration increases. It means that M is expected to decrease at a high oxygen pressure.

Let us consider a magnetic field effect on the initiation step. In the presence of an initiator (azo compound), the radicals initiating oxidation are released from the pairs $[rN_2^{\bullet}\ {}^{\bullet}r]$ and $[r^{\bullet}\ {}^{\bullet}r]$. Both pairs are born in a singlet spin state, and they recombine very fast. Since the lifetime of these pairs is much shorter than the time of spin conversion, the magnetic field effect induced by these pairs is negligible, and it can be ignored.

The initiating step in auto-oxidation is the addition of a triplet oxygen molecule to styrene to generate the biradical in a triplet state.



Hyperfine coupling with protons stimulates the spin conversion of triplet biradical into a singlet one. The latter forms an unstable peroxy molecule, which decomposes by successive O–O and C–C bond scissions, generating acetaldehyde and formaldehyde:



This channel evidently does not contribute to the initiation. However, the triplet–singlet spin conversion of the biradical competes with two reactions. The first is the addition of oxygen to the CH_2 tail of biradical (it generates a peroxy radical); the second one is the addition of a peroxy radical tail to the styrene molecule. Both reactions do contribute to the initiation. Magnetic field affects the competition of these two channels. Like in the pair $[R^{\bullet}\ {}^{\bullet}O_2R]$ triplet–singlet biradical conversion occurs along the T_+–S, T_-–S and T_0–S transitions in zero or very low magnetic fields. In high magnetic fields (0.4 T, in particular), the two transitions, T_+–S and T_-–S, are switched off, but the additional transition T_0–S induced by $\Delta g\beta H$ is switched on. Ultimately, the magnetic field retards triplet–singlet biradical conversion and decreases biradical recombination into an unstable peroxide molecule to stimulate the rate of initiation. In summary, auto-oxidation is accelerated by a magnetic field *via* increasing the initiation and decreasing the termination steps. This model predicts a decrease in M with decreasing the magnetic field in accordance with experimental data. Indeed, in a magnetic field of 0.29 T, M values do not exceed 1.05–1.20.

In conclusion, the magnetic field effects detected in this study for the first time are consistent with a generally accepted standard mechanism of the liquid phase chain oxidation of hydrocarbons. They certify two magnetically sensitive reactions of oxidation, initiation and chain termination. However, the experimental technique developed in the study may be applied to the elucidation of nonstandard oxidation mechanisms for biologically important compounds such as polyunsaturated acids, poly-conjugated and lipid molecules, in which spin-selectivity of other stages, such as $R^{\bullet} + O_2$ reaction, is implied and may be exhibited. Magnetic field is considered to be a means to detect and control spin selective stages in the oxidation mechanisms, like H/D isotope effects, and to detect spin independent chain propagation steps.[8]

This work was supported by the Russian Science Foundation (grant no. 14-23-00018).

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Received: 3rd October 2016; Com. 16/5062