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Mendeleev Commun., 2021, **31**, 341–342

Mendeleev Communications

Magnetic field effects on the initiation of chain oxidation

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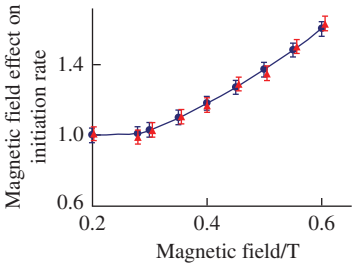
DOI: 10.1016/j.mencom.2021.05.019

The effect of a constant magnetic field on the initiation of chain oxidation at 343 K in the presence of azo initiators increases with an increase in the magnetic field strength in the range of 0.3–0.6 T and does not depend on the nature of the oxidized compound and solvent. In the case of a peroxide initiator, no magnetic field effect is observed. For azo initiators, the probability of S–T_+ and S–T_- transitions in the singlet pair [r˙ ˙r] increases, thereby enhancing the efficiency of the release of radicals from the cell.



Keywords: chain oxidation mechanism, oxygen, initiation of oxidation, magnetic field effect, unsaturated compounds, azo initiators.

A theoretical analysis of the effect of a stationary magnetic field (MF) on the detailed mechanism of radical chain oxidation of organic compounds and the obtained experimental data indicate that a magnetic field controls the stages of chain generation (initiation), chain propagation through the reaction of oxygen addition to alkyl radicals and chain termination.[1–6] Unsaturated compounds of various types are convenient models for studying initiated oxidation, the mechanism of which is described by the well-known kinetic scheme:[7]

$$\mathrm{I} \xrightarrow{+O_2,\,+RH} \mathrm{R^{\bullet}} \qquad (W_i), \qquad (1)$$

$$\mathrm{R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}} \qquad (k_1), \qquad (2)$$

$$\mathrm{RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}} \qquad (k_2), \qquad (3)$$

$$\mathrm{R^{\bullet} + R^{\bullet} \longrightarrow RR} \qquad (k_3), \qquad (4)$$

$$\mathrm{R^{\bullet} + RO_2^{\bullet} \longrightarrow ROOR} \qquad (k_4), \qquad (5)$$

$$\mathrm{RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow ROOR + O_2} \qquad (k_5), \qquad (6)$$

where I is an initiator and RH is an unsaturated compound or its saturated analog. Oxidation of vinyl compounds containing electron-donating or electron-withdrawing substituents at the carbon atom of the double bond (*e.g.*, 1,1-disubstituted alkenes $CH_2{=}C(X^1)(X^2)$, where X^1 and X^2 are groups such as H, R, COOR, Ph and CN) differs only in the radical carrying the chain. It is a polyperoxide radical, not a low-molecular one, which propagates the chain, and reaction (3) in the above scheme proceeds as the addition of this radical to the π-bond:

$$\mathrm{RO_2^{\bullet} + >C{=}C< \longrightarrow ROO(>)C{-}C^{\bullet}<} \quad (\equiv R^{\bullet}).^7 \qquad (7)$$

At temperatures of no more than 100 °C, a partial oxygen pressure in the range of 20–100 kPa and a conversion degree of no more than 1%, the reactions (4) and (5) can be excluded, and in this case, the oxidation rate W is described by the well-known equations:[7]

$$-d[O_2]/dt = W \qquad (1)$$

$$W = k_2 k_5^{-0.5} [RH] W_i^{0.5}, \qquad (2)$$

where W_i is the initiation rate.

In our previous works,[4–6] we neglected the role of initiation since in the experimental measurement of the oxidation rate, the possible effect is leveled by the dependence of W on $W_i^{0.5}$ according to equation (2). However, over a wide W_i range and with short oxidation chains, the magnetic field effect (MFE) cannot be excluded entirely. Therefore, in this work, the effect of MF on W_i was investigated using initiators of different structures.

Vinyl compounds (styrene and α-methylstyrene) and their saturated analogs (ethylbenzene and cumene), as well as compounds modeling fragments of lipid membranes (methyl oleate and methyl linoleate), were chosen as substrates for oxidation. The oxidation initiators were α,α′-azobisisobutyronitrile (AIBN), 2,2′-azobis(2,4-dimethylvaleronitrile) (AMVN) and dibenzoyl peroxide (BP). The value of W_i was determined by two methods. The first is the Kinetic Chain Initiated Reaction (KIR) method, which measures the rate of initiated oxidation and calculates W_i from equation (2) using known values of $k_2 k_5^{-0.5}$. The second is the Acceptors of Free Radicals (AFR) method, which measures the induction period of inhibited oxidation and calculates W_i using the equation:

$$W_i = f\,[InH]_0/\tau_{ind}, \qquad (3)$$

where f is the stoichiometric coefficient of inhibition, τ_{ind} is the induction period and InH is an inhibitor (Trolox) or an acceptor (TEMPO) of free radicals. The experimental data were processed using the optimization program 'Kinetika-2012'.[8] The magnitudes of the magnetic effect during initiation (MFE_i) were calculated from the ratio:

$$MFE_i = (W_i)_H/(W_i)_O, \qquad (4)$$

where $(W_i)_H$ and $(W_i)_O$ are the initiation rates in the applied magnetic field and the Earth's natural field, respectively. All the details of the experiment are given in Online Supplementary Materials.

In the absence of a magnetic field, the measured initiation rates for all investigated initiators, substrates and solvents practically coincide with the values calculated according to the

Table 1 The MFE_i values obtained by the KIR method for 50% substrate solutions in chlorobenzene at $[O_2]$ = 7.8 mM and a temperature of 343 K.

Initiator	Substrate	MFE_i at various MF strength		
		0.3 T	0.4 T	0.6 T
AIBN	Styrene	0.1	1.15	1.61
AIBN[a]		0.1[a]	1.17[a]	1.58[a]
AMVN		0.1	1.16	1.60
AIBN	Ethylbenzene	0.1	1.26	1.58
AIBN	α-Methylstyrene	0.1	1.16	1.61
AMVN		0.1	1.18	1.59
AIBN	Cumene	0.1	1.14	1.58
AMVN	Methyl linoleate	0.1	1.16	1.62
AMVN	Methyl oleate	1.0	1.17	1.58
AIBN	Chlorobenzene[b,c]	0.1	1.16	1.62
AIBN	Acetonitrile[b,c]	0.1	1.14	1.61

[a] In acetonitrile. [b] By the AFR method. [c] In an Ar atmosphere.

reference book.[9] They do not depend on the determination method, solvent and gas atmosphere (O_2 or Ar).

When using the BP initiator under the selected experimental conditions, an MFE_i is completely absent, and the measured value of W_i coincides with the value calculated from the known data.[9] For example, for styrene with [BP] = 2.1 mM, $[O_2]$ = 7.8 mM and a change in MF from 0 to 0.6 T, the MFE_i value is 1.0 ± 0.1. Similar values were obtained with other substrates, in pure chlorobenzene (in an Ar atmosphere) and also when [BP] was varied in the range of 0.1–3.2 mM (the AFR method).

The data obtained in the presence of azo initiators at various MF strength values are presented in Table 1. It can be seen that MFE_i increases with an increase in the MF strength. The MFE_i is practically the same with all substrates or in pure solvent and is independent of the determination method. The effect begins to manifest itself at MF values of more than 0.3 T, and at 0.6 T, it reaches about 1.6. This trend is illustrated in Figure 1.

We should look for an explanation of the results obtained in the differing mechanism of initiator decomposition. For azo compounds, the decomposition occurs according to the following mechanism:

$$rN{=}Nr \longrightarrow 2r^{\bullet} + N_2, \qquad (8)$$

via the formation of a geminal radical pair [r• •r].[10,11] This pair arises in a singlet spin state and, since it is short-lived, is not strongly influenced by MF. However, the hyperfine and Zeeman interactions somewhat mimic the S–T conversion, preventing recombination. As a result, the probability of radical escape from the cell increases, leading to an increase in W_i. Note that such an effect was observed, for example, during thermo- and photoinitiated radical polymerization.[12,13] A similar result was also expected when using dibenzoyl peroxide since the singlet pair [PhCOO• •Ph] performs initiation, and for this pair, both the parameter Δg and the hyperfine interaction constant are greater than 0.[14,15] However, as shown above, the MFE_i on W_i was not detected. Let us emphasize that the MFE value is small even for azo initiators. Following equation (2) at MF = 0.6 T, it increases by no more than 1.27 times ($1.6^{-0.5}$) compared to MF = 0 T. Hence, it is clear that such an increase in the determination of MFE in the published works[4,5] practically did not affect anything.

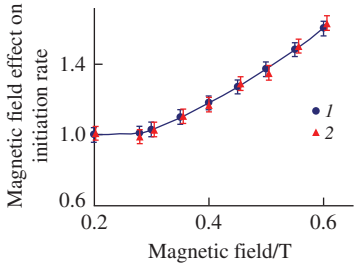


Figure 1 Dependence of the MFE_i value on the MF strength upon initiation of the oxidation of (*1*) styrene and (*2*) methyl linoleate in a 50% solution in chlorobenzene at $[O_2]$ = 7.8 mM and a temperature of 343 K.

Summing up, we can conclude that the MFE at individual stages of chain oxidation, found in this work and our previous studies,[4–6] can only be assumed as associated with radical pairs evolution since the experimental basis was the kinetic analysis of the overall rates of chain oxidation. Possibly, the effect may be caused by 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. Although the developed methodology refers to liquid-phase reactions, it can be used to study an MFE on the oxidation of biologically significant compounds in multiphase systems such as micelles, liposomes and membranes.

This work was supported by the Russian Science Foundation (grant no. 20-13-00148). The authors are grateful to P. G. Demidov Yaroslavl State University (grant no. AAAA-A19-119111290038-4) for financial support in designing and creating the experimental setup. The stable nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was kindly provided by Dr. V. D. Sen' (IPCP RAS).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.019.

References

1 A. L. Buchachenko, *Magneto-Biology and Medicine*, Nova Science Publishers, New York, 2014.
2 C. Sampson, R. H. Keens and D. R. Kattnig, *Phys. Chem. Chem. Phys.*, 2019, **21**, 13526.
3 N. N. Lukzen, K. L. Ivanov, V. M. Sadovsky and R. Z. Sagdeev, *J. Chem. Phys.*, 2020, **152**, 34103.
4 E. M. Pliss, A. M. Grobov, A. K. Kuzaev and A. L. Buchachenko, *Mendeleev Commun.*, 2017, **27**, 246.
5 E. M. Pliss, A. M. Grobov, A. K. Kuzaev and A. L. Buchachenko, *J. Phys. Org. Chem.*, 2019, **32**, e3915.
6 E. M. Pliss, A. M. Grobov, A. K. Kuzaev and A. L. Buchachenko, *Mendeleev Commun.*, 2020, **30**, 433.
7 E. T. Denisov and I. B. Afanas'ev, *Oxidation and Antioxidants in Organic Chemistry and Biology*, CRC Press, Boca Raton, 2005.
8 A. V. Sokolov, S. V. Popov, E. M. Pliss and D. V. Loshadkin, *Computer Programs. Databases. Topographies of Integrated Circuits*, 2013, 2013612187 (in Russian).
9 E. T. Denisov, T. G. Denisova and T. S. Pokidova, *Handbook of Free Radical Initiators*, John Wiley & Sons, Hoboken, NJ, 2003.
10 K. M. Salikhov, Yu. N. Molin, R. Z. Sagdeev and A. L. Buchachenko, *Spin Polarization and Magnetic Effects in Radical Reactions*, ed. Yu. N. Molin, Elsevier, Amsterdam, 1984.
11 H. Hayashi, *Introduction to Dynamic Spin Chemistry: Magnetic Field Effects on Chemical and Biochemical Reactions*, World Scientific Publishing Co., Singapore, 2004.
12 I. V. Khudyakov, N. Arsu, S. Jockusch and N. J. Turro, *Des. Monomers Polym.*, 2003, **6**, 91.
13 I. Rintoul, *Processes*, 2017, **5**, 15.
14 R. A. Cooper, R. G. Lawler and H. R. Ward, *J. Am. Chem. Soc.*, 1972, **94**, 552.
15 P. S. Engel, *Chem. Rev.*, 1980, **80**, 99.

Received: 29th December 2020; Com. 20/6410