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Effect of acetonitrile on the catalytic decomposition of hydrogen peroxide by vanadium ions and conjugated oxidation of alkanes

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The rate of hydrogen peroxide decomposition in acetonitrile in the presence of a vanadate anion and pyrazine-2-carboxylic acid decreases remarkably when alkane (cyclohexane, *n*-heptane, isooctane) is added to the reaction solution. The alkane added is oxidized by this system to alkyl hydroperoxide. This is explained by the fact that much more hydrogen peroxide molecules are consumed to acetonitrile oxidation with formation of the final products, which is suppressed considerably by additives of necessary amounts of alkane, than those consumed to the oxidation of cyclohexane to form cyclohexyl hydroperoxide. In an organic solvent, H_2O_2 decomposes in a non-chain radical process.

Key words: metallocomplex catalysis, oxidation, hydrogen peroxide, vanadium complexes, alkanes, C—H bond activation.

It is known[1—3] that in an aqueous solution the photochemical decomposition of hydrogen peroxide and many reactions of its catalytic decomposition by ions and complexes of transition metals are chain-radical processes. In these processes, chain mediators are, in particular, hydroxyl ($HO^\bullet$) and hydroperoxyl ($HO_2^\bullet$) radicals. Chain propagation steps in the photochemical process are described by the following reactions:

$$HO^\bullet + H_2O_2 \longrightarrow H_2O + HO_2^\bullet, \tag{1}$$

$$HO_2^\bullet + H_2O_2 \longrightarrow HO^\bullet + O_2 + H_2O. \tag{2}$$

Transition metal ions (M^{n+}) often catalyze reaction (2) in addition to their involvement in the chain initiation step

$$HO_2^\bullet + M^{n+} \longrightarrow H + O_2 + M^{(n-1)+}, \tag{3}$$

$$M^{(n-1)+} + H_2O_2 \longrightarrow M^{n+} + HO^- + HO^\bullet. \tag{4}$$

The addition of some organic substances to these systems decreases the rate of hydrogen peroxide decomposition without changing the initiation rate. This is related to a change in the mechanism of chain termination: the interaction of the organic substance with hydroxyl radicals results in the formation of secondary radicals that are less reactive in chain propagation steps but are efficient in chain termination processes. The degree of suppression of a chain process should depend on the reactivity of secondary radicals. Only in the case where they are inactive in chain propagation reactions, the chain process is suppressed completely, and the rate of organic substance oxidation corresponds to the initiation rate. Hydrogen peroxide decomposition is inhibited in an aqueous solution, as a rule, at concentrations of organic substances much lower than the H_2O_2 concentration due to their higher reactivity (compared to H_2O_2) toward $HO^\bullet$ radicals and to the chain character of decomposition.

Evidently, in an organic solvent, whose molecules, as a rule, interact rather efficiently with hydroxyl radicals, chain processes of hydrogen peroxide decomposition are impeded by a conjugated process of solvent oxidation. This also concerns chain-radical reactions of decomposition of organic peroxides and any radical reactions in which free radicals that formed can interact with solvent molecules. Therefore, it seemed of interest to analyze the decomposition of hydrogen peroxide by vanadium(v) ions in acetonitrile producing hydroxyl radicals.[4—9]

We showed that the initial rate of decomposition of hydrogen peroxide (0.5 mol L^{-1}), introduced into acetonitrile as a 38% aqueous solution, at 50 °C in the presence of catalyst $Bu^n{}_4NVO_3$ ($5 \cdot 10^{-4}$ mol L^{-1}) and cocatalyst pyrazine-2-carboxylic acid (PCA; $2.5 \cdot 10^{-3}$ mol L^{-1}) is equal to $2 \cdot 10^{-4}$ mol L^{-1} s^{-1}. Under these conditions, the rate of molecular oxygen evolution is $0.6 \cdot 10^{-4}$ mol L^{-1} s^{-1}. Therefore, hydrogen peroxide is consumed to the oxidation of components of the reaction solution with a rate of $0.8 \cdot 10^{-4}$ mol L^{-1} s^{-1}. The oxidation of the solution components during the reaction is indicated by the formation of such products as formaldehyde, CO, and formic acid. Their yield increases with the reaction time[8] but remains low. Other oxidation products were not identified. Two substances that can be oxidized under these conditions are PCA and acetonitrile. Taking

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into account that the oxidizing effect of the system considered is caused by the generation of hydroxyl radicals, it should be assumed that acetonitrile is mainly oxidized. Indeed, even accepting that the rate constant of the reaction of PCA with $HO^{\bullet}$ is $1.0 \cdot 10^{10}$ L mol^{-1} s^{-1}, we have that the ratio of the reaction rates of $HO^{\bullet}$ with PCA and MeCN does not exceed 0.07, because it is known[10] that $k(HO^{\bullet} + MeCN) = 2.2 \cdot 10^7$ L mol^{-1} s^{-1}. In fact, it is likely that $k(HO^{\bullet} + PCA) < 1.0 \cdot 10^{10}$ L mol^{-1} s^{-1}.

We previously[9] took into account the possibility of withdrawing hydroxyl radicals by acetonitrile when analyzed the influence of the initial concentration of cyclohexane (CyH) on the rate of formation of cyclohexyl hydroperoxide (CyOOH). The analysis was based on assumptions that the presence of cyclohexane exerts no effect on the rate of hydroxyl radical generation, and secondary radicals formed from CyH and acetonitrile are not involved in the chain decomposition of hydrogen peroxide. This analysis allowed us to conclude that at a high cyclohexane concentration the rate of formation of cyclohexyl hydroperoxide tends to the rate of generation of hydroxyl radicals by the system, *i.e.*, to the initiation rate. If these assumptions are valid, then CyH additives should not affect the rate hydrogen peroxide decomposition. However, our experiments showed that cyclohexane additives decrease the rate of hydrogen peroxide decomposition under the above-indicated conditions. For instance, in the presence of cyclohexane (0.46 mol L^{-1}), the rates of H_2O_2 decomposition and O_2 evolution decrease to $0.9 \cdot 10^{-4}$ and $1.5 \cdot 10^{-5}$ mol L^{-1} s^{-1}, respectively, from $2 \cdot 10^{-4}$ and $6 \cdot 10^{-5}$ mol L^{-1} s^{-1} in its absence. In this case, the rate of formation of the main oxidation product (cyclohexyl hydroperoxide) is equal to $1.5 \cdot 10^{-5}$ mol L^{-1} s^{-1}, which is 70% of the initiation rate.[9,11] With an increase in the initial concentration of CyH, the rate of dioxygen evolution tends to zero, and the rate of hydrogen peroxide decomposition tends to a doubled rate of CyOOH formation, *i.e.*, the empirical reaction of catalytic cyclohexane oxidation corresponds to the equation

$$2\,H_2O_2 + CyH = 2\,H_2O + CyOOH. \qquad (5)$$

These data show that the oxidation of one acetonitrile molecule induced by hydroxyl radicals results in the decomposition of about ten H_2O_2 molecules, 50% of which are consumed to the oxidation of MeCN, and the second half is consumed to H_2O_2 decomposition accompanied by molecular oxygen evolution. It should be noted that the additional consumption of hydrogen peroxide in the oxidation of MeCN cannot be related to the induction of chain H_2O_2 decomposition by radicals formed from acetonitrile. In fact, if the radicals formed from MeCN induce the chain decomposition of hydrogen peroxide involving $HO^{\bullet}$ radicals, then the rate of removal of hydroxyl radicals from the process due to their interaction with acetonitrile would be lower than the rate calculated as

$$W_{MeCN} = k(HO^{\bullet} + MeCN) \cdot [MeCN] \cdot [HO^{\bullet}], \qquad (6)$$

because of $HO^{\bullet}$ regeneration in subsequent steps. In this case, one of the main assumption of the scheme of competitive interaction of hydroxyl radicals with MeCN and cyclohexane would be violated.[9] Therefore, first, the ratio of rate constants

$$k(HO^{\bullet} + MeCN)/k(HO^{\bullet} + CyH), \qquad (7)$$

determined by the competitive method from the plot of the rate of cyclohexyl hydroperoxide formation *vs.* cyclohexane concentration should be lower than the ratio calculated from the radiation chemical data on the rate constants of the reactions of $HO^{\bullet}$ with these substrates. Second, a difference between ratio (7) determined in photochemical (in the absence of catalyst) and catalytic (in the presence of catalyst) experiments should be expected, because the involvement of a catalyst in the chain propagation cycle seems highly probable. Third, the experimental dependence of the rate of cyclohexyl hydroperoxide formation on the cyclohexane concentration should not correspond, generally speaking, to the dependence predicted in the framework of the simplest competitive model.[9] In fact, the ratio of constants corresponds to that calculated from the radiation chemical data. Since this ratio is almost the same for photochemical and catalytic experiments,[11] we can assert that the experimental data correspond to the simplest competitive scheme. Therefore, we believe that the additional consumption of hydrogen peroxide for acetonitrile oxidation to final products is not related to the induction of chain H_2O_2 decomposition by radicals formed from MeCN. This chain decomposition is accompanied by the generation of $HO^{\bullet}$ radicals.

Since in acetonitrile the rate of possible chain propagation (1) is much lower that the rate of the reaction of $HO^{\bullet}$ radicals with MeCN (*i.e.*, chain termination rate), the catalytic decomposition of hydrogen peroxide by vanadium ions is a radical but not chain process. The main channel of O_2 evolution in the reaction is presented by secondary processes of acetonitrile oxidation by hydrogen peroxide, because the rate of O_2 evolution decreases with a decrease in the rate of acetonitrile oxidation. Under the conditions studied ($[Bu^n{}_4NVO_3] = 5 \cdot 10^{-4}$ mol L^{-1}, $[PCA] = 2.5 \cdot 10^{-3}$ mol L^{-1}, $[H_2O_2] = 0.5$ mol L^{-1}, 50 °C), in the absence of cyclohexane additive, a high consumption of H_2O_2 calculated to oxidized MeCN molecule is observed. Additives of CyH decrease considerably the consumption of H_2O_2 followed by the formation of the target product of alkane oxidation, *viz.*, CyOOH. This is demonstrated by the presented below results of experimental measurements and estimation calculations of the rate of hydrogen peroxide decomposition ($W_{H_2O_2}$) and cyclohexane oxidation (W_{CyH}) at different alkane concentrations. For example, at [CyH] = 0.92 mol L^{-1} and using 38% H_2O_2 in the initial reaction period, approximately a half of the whole amount of H_2O_2 is consumed to the oxidation of CyH, whereas the second half is consumed to the oxidation of MeCN and formation of O_2.

$[\mathrm{CyH}]_0$ /mol L^{-1}	$W_{H_2O_2} \cdot 10^4$	$W_{\mathrm{CyH}} \cdot 10^4$
	mol L^{-1} s^{-1}	
0	2.0	0
0.46	0.9	0.15
0.92	0.7	0.175
1.84	0.6	0.19

At a high cyclohexane concentration, acetonitrile, being an acceptor of $HO^{\bullet}$ radicals, effects neither the rate of H_2O_2 decomposition, nor the rate of cyclohexane oxidation. Taking into account the stoichiometry of cyclohexane oxidation (Eq. (5)) and the fact that cyclohexyl hydroperoxide is not formed**[9]** when argon is vigorously passed through the reaction solution (*i.e.*, in the absence of O_2), one should accept that oxygen necessary for the reaction is formed in required amounts when hydrogen peroxide decomposes in the catalytic cycle. Based on this, we can propose a mechanism of hydrogen peroxide decomposition and cyclohexane oxidation at a high concentration of the latter when all hydroxyl radicals formed interact with alkane (Eqs (8)—(16)).

$$V^{5+} + H_2O_2 \rightleftharpoons \text{Complex} \quad (8)$$

$$\text{Complex} \longrightarrow V^{4+} + H^+ + HO_2^{\bullet} \quad (9)$$

$$V^{5+} + HO_2^{\bullet} \longrightarrow V^{4+} + H^+ + O_2 \quad (10)$$

$$V^{4+} + H_2O_2 \longrightarrow V^{5+} + HO^- + HO^{\bullet} \quad (11)$$

$$HO^{\bullet} + \mathrm{CyH} \longrightarrow H_2O + \mathrm{Cy}^{\bullet} \quad (12)$$

$$\mathrm{Cy}^{\bullet} + O_2 \longrightarrow \mathrm{CyOO}^{\bullet} \quad (13)$$

$$\mathrm{CyOO}^{\bullet} + V^{4+} + H^+ \longrightarrow \mathrm{CyOOH} + V^{5+} \quad (14)$$

$$\mathrm{CyOO}^{\bullet} + \mathrm{HOO}^{\bullet} \longrightarrow \mathrm{CyOOH} + O_2 \quad (15)$$

$$\mathrm{CyOO}^{\bullet} + H_2O_2 \longrightarrow \mathrm{CyOOH} + \mathrm{HOO}^{\bullet} \quad (16)$$

The formation of CyOOH in reaction (15) cannot be excluded, and reaction (16) is hardly possible. First, its rate constant is low. Second, if this reaction occurs, then the chain process of CyOOH formation should inevitably proceed through the sequence of steps (10)—(13), which contradicts the main assumption of the scheme of competitive interaction of hydroxyl radicals with acetonitrile and cyclohexane.**[9]** The latter scheme satisfactorily describes the experimental data.**[9]**

We found that other alkanes, *viz.*, *n*-heptane and isooctane (2,2,4-trimethylpentane), similarly affect the process. Additives of these hydrocarbons suppress cyclohexane oxidation (the initial rate of CyH oxidation decreases by ~3 times). The influence of an isooctane additive on the yield of CyOOH can be described by the simplest competitive scheme assuming that secondary radicals are not involved in H_2O_2 decomposition. An analysis of the obtained experimental data made it possible to determine the ratio of rate constants

$$k(HO^{\bullet} + \text{isooctane})/k(HO^{\bullet} + \mathrm{CyH}) = 1.16 \pm 0.06,$$

which agrees well with the parameter calculated from the radiation chemical experiments (1.15).**[10]**

It is of interest that methanol additives decrease the rate of hydrogen peroxide decomposition to a noticeably less extent than alkanes do. For example, when its concentration is 0.5 mol L^{-1}, the rate of H_2O_2 decomposition decreases only by 30%. The reason for this phenomenon is not related to the difference of rate constants of the reactions of $HO^{\bullet}$ radicals with MeOH and cyclohexane. Indeed, the rate constants of these reactions are close**[10]**: $(8.4 \pm 1.7) \cdot 10^8$ and $1.25 \cdot 10^9$ L mol^{-1} s^{-1}, respectively. A less efficient decrease in the rate of hydrogen peroxide decomposition by methanol additives compared to alkanes is caused, most likely, by the fact that the radicals formed from MeOH induce the chain process of H_2O_2 decomposition involving hydroxyl radicals (see, in particular, reactions (1) and (2)), which cannot be done by saturated hydrocarbons.

Thus, based on the obtained results, we can conclude that the decomposition of hydrogen peroxide in the organic solvent (acetonitrile) with formation of hydroxyl radicals proceeds *via* the non-chain radical mechanism.

Experimental

Experiments were carried out in glass cylindrical vessels temperature-controlled using water jackets. Reactions were carried out at 50 °C in air (no special protection from air penetration into a reaction vessel was carried out). The volume of a reaction solution was 5 mL. Samples of the reaction solution (0.2 mL) were taken at certain time intervals, treated with excess solid triphenylphosphine for 10 min, and analyzed by GLC. After the solution was reduced with triphenylphosphine, alkyl hydroperoxide converted to the corresponding alcohol in ~100% yield. An LKhM-80-6 chromatograph (columns 2 m long containing 5% Carbowax 1500 on Inerton AW-HMDS (0.25—0.315 mm); argon as carrier gas) was used. In experiments determining the rate of molecular oxygen evolution, the volume of the evolved gas was measured by the volumetric method. The concentration of H_2O_2 was determined spectrophotometrically after addition of titanium(IV) sulfate.**[12]**

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References

1. S. Lunak and P. Sedlák, *J. Photochem. Photobiol. A: Chem.*, 1992, **68**, 1.
2. A. N. Ermakov, Yu. N. Kozlov, and A. P. Purmal´, *Kinet. Katal.*, 1999, **40**, 663 [*Kinet. Catal.*, 1999, **40** (Engl. Transl.)].
3. A. Ya. Sychev and G. G. Duka, *Fundamental´nye i prikladnye aspekty gomogennogo kataliza metallokompleksami*, Moldavskii Gos. Univ., Kishinev, 2002, Part 1, 3 (in Russian).
4. A. E. Shilov and G. B. Shul´pin, *Chem. Rev.*, 1997, **97**, 2879.
5. A. E. Shilov and G. B. Shul´pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers, Dordrecht—Boston—London, 2000, Ch. X, 430.
6. G. B. Shul´pin, D. Attanasio, and L. Suber, *J. Catal.*, 1993, **142**, 147.
7. M. C. Guerreiro, U. Schuchardt, and G. B. Shul´pin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 780 [*Russ. Chem. Bull.*, 1997, **46**, 749 (Engl. Transl.)].
8. G. Süss-Fink, G. V. Nizova, S. Stanislas, and G. B. Shul´pin, *J. Mol. Catal. A: Chem.*, 1998, **130**, 163.
9. G. B. Shul´pin, Yu. N. Kozlov, G. V. Nizova, G. Süss-Fink, S. Stanislas, A. Kitaygorodskiy, and V. S. Kulikova, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1351.
10. A. K. Pikaev and S. A. Kabakchi, *Reaktsionnaya sposobnost´ pervichnykh produktov radioliza vody. Spravochnik* [*Reactivity of Primary Products of Water Radiolysis*], Energoizdat, Moscow, 1982, 3 (in Russian).
11. Yu. N. Kozlov, L. Gonzalez-Cuervo, G. Süss-Fink, and G. B. Shul´pin, *Zh. Fiz. Khim.*, 2003, **77**, 652 [*Russ. J. Phys. Chem.*, 2003, **77**, 575 (Engl. Transl.)].
12. G. Charlot, *Les Methodes de la Chimie Analytique. Analyse Quantitative Minerale*, Masson et C^{ie}, Ed´iteurs, Paris, 1961.

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