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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Decomposition of Hydrogen Peroxide in Protic and Polar Aprotic Solvents on TS-1 Heterogeneous Catalyst

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Abstract—Kinetic parameters of H_2O_2 decomposition in methanol, propanol-1, propanol-2, acetone, and acetonitrile at 30–55°C on a TS-1 heterogeneous catalyst were determined. Recommendations are given on choice of solvents in oxidation of organic compounds with hydrogen peroxide.

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In the last 20 years, a large number of studies devoted to the liquid-phase oxidation of organic compounds by molecular and(or) bound oxygen and, in particular, hydrogen peroxide, to hydroxylation on heterogeneous micro- and mesoporous titanium-silicalite catalysts, and to synthesis and structural analysis of a catalyst were reported [1–4]. At present, highly selective processes for liquid-phase oxidation of “small” molecules with an aqueous solution on hydrogen peroxide on a TS-1 silicalite catalyst are known, such as epoxidation of propylene to propylene oxide, hydroxylation of phenol to hydroquinone and pyrocatechol, ammoximation of cyclohexanone to oxime, and oxidation of alkenes and alcohols. TS-1 catalyst has a crystal structure of the type of ZSM-3 zeolite with a 3D system of channels 5.3–5.6 Å in diameter, with a part of silicon atoms isomorphically substituted with titanium(IV) ions.

The liquid-phase oxidation with hydrogen peroxide on TS-1 is, as a rule, performed in the presence of protic and aprotic solvents: low-molecular-mass alcohols and carbonyl compounds, e.g., methanol, tertiary butanol, acetone, acetonitrile, and their mixtures with water [5, 6], whose role in the chemical process remains unclear.

By analogy with the homogeneous metal-complex catalysis, various schemes are suggested for activation of bound oxygen (in particular, that in H_2O_2 and ROOH) and its involvement in the mechanism of substrate oxidation on titanium(IV) active centers. Unfortunately, these schemes can only be regarded as working hypotheses. It should also be noted that these schemes disregard the influence exerted by the solvent on the selectivity of the oxidation process.

Our communication presents experimental data on the decomposition kinetics of hydrogen peroxide and formation selectivity of molecular oxygen in an excess amount of lower alcohols (methanol, propanol-1, propanol-2, acetone, acetonitrile, and their mixtures with water) in the presence of TS-1 catalyst.

EXPERIMENTAL

We used the following reagents: methanol [chemically pure, 99.5%, GOST (State Standard) 6995–77], propanol-1 [chemically pure, TU (Technical Specification) 6-09-4344–77], propanol-2 (chemically pure, TU 2632-015-11291058–95), acetone (analytically pure, GOST 2603–79), acetonitrile (chemically pure, 99.85%, TU SOMR2-040–06), and 35% aqueous solution of hydrogen peroxide. TS-1 catalyst was produced by the method described in [1] and had the following characteristics: TiO_2 content 2.6%, specific micropore volume 0.140 cm^3 g^{-1}, and average particle size 10–100 μm (determined with a GSM-35CF scanning electron microscope. An X-ray diffraction analysis demonstrated that there is no anatase phase in TS-1.

Experiments were carried out in a thermostated glass reactor in an excess of a solvent with permanent shaking, which provided that the reaction occurred under kinetic control. In all the experiments, the volume of the reaction mixture remained constant (10 ml) at varied initial conditions: initial H_2O_2 concentration 0.3–1.2 M, catalyst amount 0.25–1.0 g, and temperature 30–55°C.

The content of substances in solution was analyzed by the following methods: hydrogen peroxide, by iodometric titration; formaldehyde formed in oxidation of methane, with an M 907-10 photocolorimeter; and propionic aldehyde and acetone formed in oxidation of, respectively, propanol-1 and propanol-2, with Tsvet 800 chromatograph (flame-ionization detector, APIESON L fixed phase, carrier gas N_2, 30 ml min^{-1}, $T = 80°C$).

The molecular oxygen released in the course of oxidation was determined volumetrically at a temperature of 20 ± 0.1°C under atmospheric pressure.

It was noted in [1, 8] that, with TS-1 crystalline particles less than 300 μm in size, organic compounds are oxidized by hydrogen peroxide under kinetic control with high selectivity. The kinetic control over the reaction was provided by using TS-1 catalyst with a particle size not exceeding 100 μm under vigorous agitation of the reaction solution.

In oxidation of methanol, propanol-1, and propanol-2 with hydrogen peroxide in the liquid phase on TS-1 at 35–55°C in the course of 4–6 h, mostly formaldehyde, propionic aldehyde, and acetone, respectively, were formed. The formation of other oxygen-containing compounds, noted in [9], did not exceed 9%. In decomposition of hydrogen peroxide, oxygen accumulated in the gas phase, with the selectivity of this process primarily dependent on the nature of a substrate being oxidized and, to a lesser extent, on temperature (Table 1).

As can be seen in Table 1, the selectivity with respect

Table 1. Hydrogen peroxide conversion $X_{H_2O_2}$ and oxygen formation selectivity $\Phi_{O_2}^{H_2O_2}$

Substrate	Content of TS-1, g	$c_{H_2O_2}$, M	T, °C	$X_{H_2O_2}$, %	$\Phi_{O_2}^{H_2O_2}$, %
Methanol	0.5	0.65	45	28	28
	0.5	0.90	45	33	29
	0.8	0.37	50	66	24
Methanol + 5 vol% H_2O	0.5	0.67	45	30	35
Methanol + 0.1 N HCl, pH 1.84	0.5	0.57	40	20	35
Methanol + 0.1 N HCl, pH 0.92	0.5	0.57	40	32	40
Propanol-1	0.2	0.60	45	72	3
	0.5	0.62	45	74	3
Propanol-2	0.5	0.60	40	100	4
	0.5	0.60	45	100	4
Acetone	0.5	0.65	45	25	14
	0.8	0.37	50	40	13
Acetone + 20 vol% H_2O	0.5	0.69	45	29	16
	0.8	0.35	45	45	18
	0.8	0.35	50	67	28
	0.8	0.35	55	78	31
Acetonitrile	0.5	0.65	45	60	30
	0.8	0.37	50	72	26

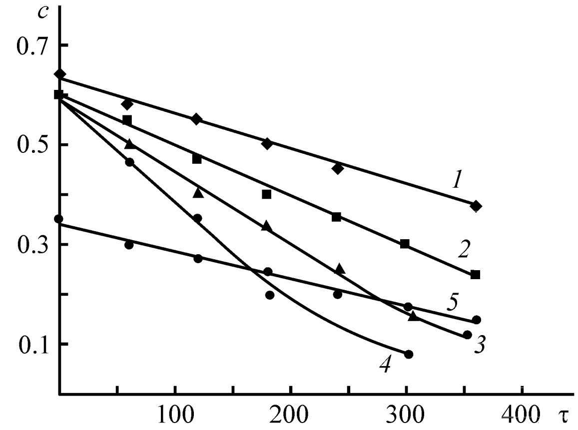


Fig. 1. Kinetics of H_2O_2 consumption in (*1–4*) methanol and (*5*) acetone at 45°C. (*c*) Hydrogen peroxide concentration and (τ) time; the same for Figs. 2 and 3. Initial H_2O_2 concentration (M): (*1*) 0.64, (*2–4*) 0.6, and (*5*) 0.35. TS-1 catalyst (wt %): (*1*) 2.5, (*2*) 5.0, (*3*) 7.5, (*4*) 10.0, and (*5*) 8.0.

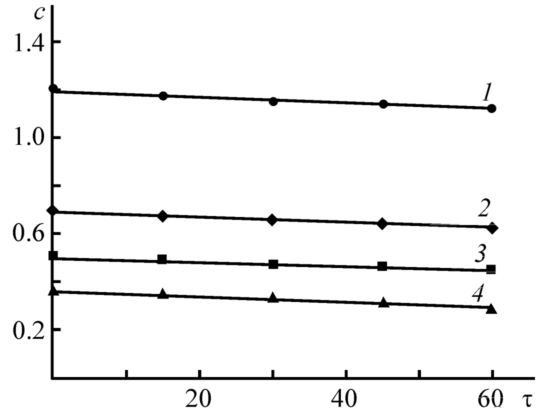


Fig. 2. Kinetics of H_2O_2 consumption in acetone. Content of TS-1 catalyst 8.0 wt %, temperature 50°C. Initial H_2O_2 concentration (M): (*1*) 1.2, (*2*) 0.7, (*3*) 0.5, and (*4*) 0.35.

to O_2 at the decomposition point of H_2O_2 (40–50°C) depends on the nature of a substrate (solvent) and varies in the order propanol-2 > propanol-1 > acetone > acetonitrile ≥ methanol.

Presence of water leads to an increase in selectivity. For example, in decomposition of H_2O_2 at 45°C in methanol and acetone, the selectivity with respect to O_2 was 28 and 14%, respectively; and that in water–methanol (molar ratio $CH_3OH : H_2O = 0.8$) and water–acetone (molar ratio $C_3H_6O : H_2O = 1$) solutions increased by 6 and 9%, respectively. The increase in selectivity is noticeably affected by the acidity of the medium. The selectivity of O_2 formation increased with the acidity of the medium.

The selectivity of O_2 formation in decomposition of H_2O_2 is hardly affected by a protic (methanol) or polar aprotic solution (acetonitrile, acetone per methyl group) or by the dielectric constant of the medium ($\varepsilon_{C3H6O} = 20.7$, $\varepsilon_{CH3OH} = 32.7$, $\varepsilon_{CH3CN} = 38.8$). The kinetics of H_2O_2 decomposition was studied in anhydrous and aqueous solutions of substrates (alcohols, acetone, acetonitrile) at various amounts of TS-1 catalyst, H_2O_2 concentrations, and temperatures.

Figures 1–3 show kinetic curves of H_2O_2 consumption in methanol, acetone, propanol-1, and propanol-2. It was found that the decomposition of H_2O_2 at a conversion not exceeding 50% in methanol and higher than 80% in acetone occurs by the zeroth-order reaction at a constant rate, irrespective of the reaction products. Using the method of initial concentrations at $c_{H2O2} = 0.35–1.2$ M, we confirmed the zeroth order with respect to hydrogen peroxide: the initial rate of H_2O_2 decomposition is independent of the concentration of hydrogen peroxide (parallel straight lines in Fig. 2). In this case, the specific rate of the reaction, i.e., the reaction rate related to unit mass of the catalyst, is independent of the amount of TS-1 in the reaction volume. It was found that introduction of water into methanol and acetone to a concentration of 6 M hardly affects the consumption kinetics of hydrogen peroxide at 40°C. Addition of 11 M of water weakly hinders the decomposition of H_2O_2 in the case of methanol, and, by contrast, accelerates the chemical process (by approximately 15–20%) in the case of acetone.

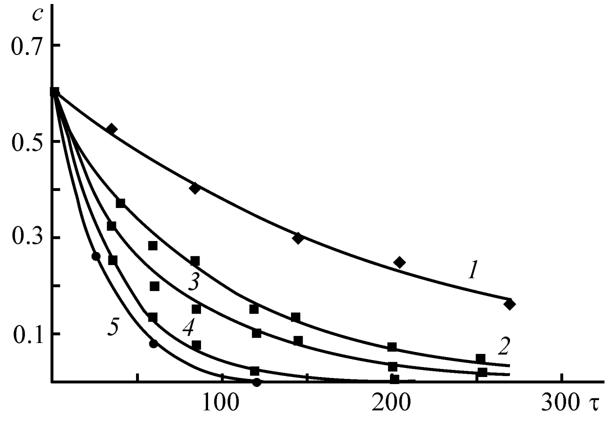


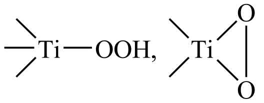
Fig. 3. Kinetics of H_2O_2 consumption in (*1–4*) propanol-1 and (*5*) propanol-2. Initial H_2O_2 concentration 0.6 M. TS-1 catalyst (wt %): (*1*) 2.0, (*2*) 5.0, (*3*) 7.5, (*4*) 10.0, and (*5*) 5.0. Temperature (°C): (*1–4*) 45 and (*5*) 40.

The consumption of H_2O_2 in propanol-1 is slower than that in propanol-2 (Fig. 3, curves *2* and *5*). The reaction

Table 2. Kinetic parameters of H_2O_2 decomposition in alcohols, acetone, and acetonitrile at 45–55°C

Substrate	T, °C	$\lvert\log k\rvert$ (k, mol g–1 min^{-1})	$\log k_0$	E, kJ mol^{-1}
Methanol	55	4.11	7.35	72 ± 5
Propanol-1	55	3.74	3.87	48 ± 5
Propanol-2	50	3.45	2.73	38 ± 5
Acetone	55	4.85	9.03	87 ± 5
Acetonitrile	45	4.62	1.97	40 ± 5

has zeroth order with respect to H_2O_2 at conversions lower than 50%, which was also demonstrated by the method of initial concentrations. Further, with increasing depth of H_2O_2 decomposition, the reaction becomes slower. The deceleration effect is presumably due to chemisorption of H_2O_2, propanol-1, propanol-2, and H_2O on titanium(IV) active centers in TS-1 catalyst [9]. As H_2O_2 is consumed, the surface concentration of active titanium-hydroperoxide and peroxide centers



[10] decreases because the substrate (alcohol), present in the reaction mass in a large excess, is sorbed on Ti(IV). Consequently, if we consider the chemical process of hydrogen peroxide conversion involving the substrate (alcohol, acetone, acetonitrile) on the titanium(IV) active center to be the rate-determining stage, we can understand why the decomposition of H_2O_2 is hindered in the presence of a substrate "active" toward adsorption. The reaction rate can be expressed by the formula

$$r = \frac{K_{\mathrm{eff}} c_{H_2O_2} c_s}{1 + b_{H_2O_2} c_{H_2O_2} + b_{H_2O_2} c_{H_2O_2} b_s c_s + b_s c_s + b_s c_s + b_{H_2O} c_{H_2O}},$$

where k_{eff} is the effective rate constant of H_2O_2 consumption; $b_{H_2O_2}$, b_s, and b_{H_2O}, adsorption coefficients of H_2O_2, substrate, and water, respectively; and $c_{H_2O_2}$, c_{H_2O}, and c_s, concentrations of H_2O_2, water, and substrate (solvent), respectively.

At $c_{H_2O_2} b_{H_2O_2} >> 1 + b_s c_s + b_{H_2O} c_{H_2O}$, the reaction rate is independent of the H_2O_2 concentration (zeroth order) and has the maximum value. At $c_{H_2O_2} b_{H_2O_2} << 1 + b_s c_s + b_{H_2O} c_{H_2O}$, the reaction is hindered by the substrate (solvent) and is described by the kinetic equation

$$r = \frac{K_{\mathrm{eff}} c_{H_2O_2} c_s}{1 + b_s c_s + b_{H_2O} c_{H_2O}}.$$

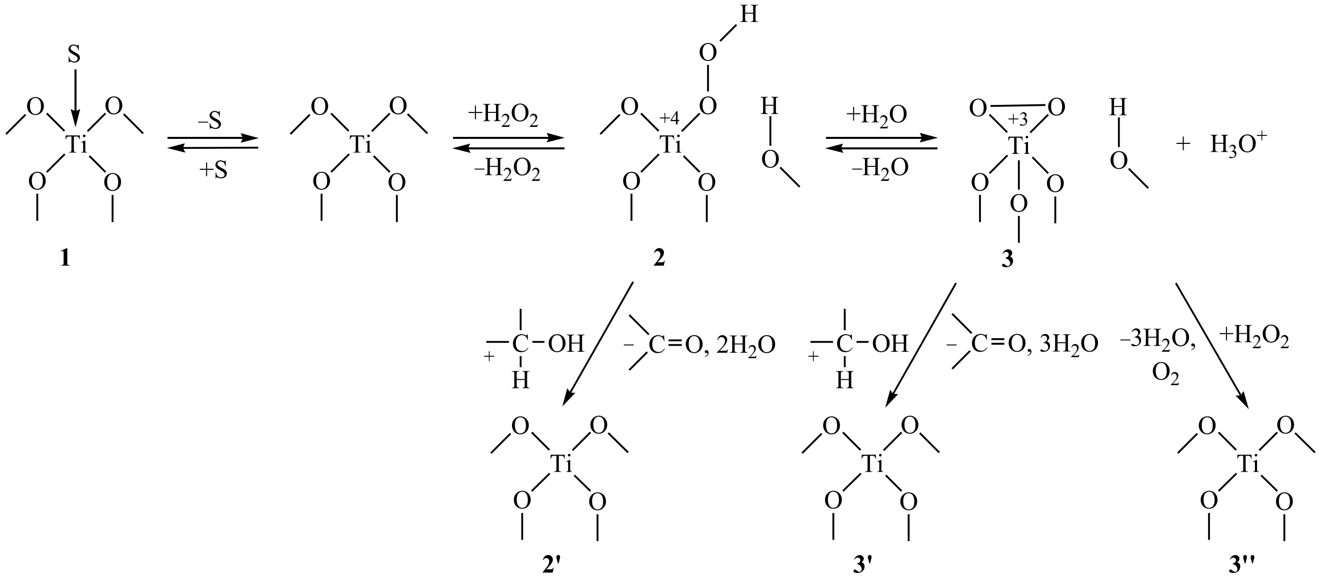
It was shown in [6] that water is inferior in adsorption on the hydrophobic catalyst TS-1 to organic substances.

Kinetic studies also demonstrated that the decomposition rate of H_2O_2 in alcohols and acetone grows with increasing temperature in the range 30–50°C. The expression for the rate constant of the reaction, found from the initial rate of H_2O_2 consumption, is satisfactorily described by the Arrhenius dependence on inverse temperature. The dependence is linearized in the coordinates $\log k$–$1/T$, with its slope ratio equal to the activation energy E. The results of the corresponding calculations are listed in Table 2.

The solvents under study can be arrange in order of decreasing reactivity of H_2O_2 on as follows: propanol-2 > propanol-1 > acetonitrile > methanol > acetone.

Analysis of the kinetic data shows that the rate of H_2O_2 decomposition on TS-1 is for the most part affected by energy characteristics of bonds ruptured and formed in conversion of the titanium(IV)–H_2O_2–substrate complex. The type of a solvent (protic or polar aprotic), dielectric constant of the medium (aqueous-organic solutions) affect the rate and pathway of H_2O_2

Scheme.



decomposition into O_2 and products formed in oxidation of the substrate (solvent) to a lesser extent.

Based on our experimental data and taking into account the published evidence, we can represent the mechanism of H_2O_2 decomposition on TS-1 in protic and polar aprotic organic solvents (reagents) by the scheme.

The formation of complex **2** and the role played by water in the equilibrium reaction between complexes **2** and **3** were demonstrated in [10]. A rapid adsorption of the substrate (solvent) and chemisorption of hydrogen peroxide occurs in pores of the microporous catalyst TS-1 on titanium(IV) active centers to give complexes substrate (solvent)–titanium(IV) (**1**), hydroperoxide–titanium(IV) (**2**), and peroxide–titanium(IV) (**3**) [1, 9–11]. Equilibrium is attained between complexes **2** and **3**.

Further, complexes **2** and **3** enter into redox reactions with the substrate or hydrogen peroxide to give oxidation products (channels **2'**, **3'**) and molecular oxygen (channel **3''**). The relative contributions of reactions by the channels are determined by the reactivities of the molecules of a substrate and hydrogen peroxide, possibly incident from the bulk or sorbed on titanium(IV) active centers. It is significant that, with increasing activation energy of H_2O_2 decomposition, the selectivity of substrate oxidation decreases and the yield of molecular oxygen grows.

In [1, 12, 13], a radical homolytic mechanism of oxidation of organic compounds by hydrogen peroxide via channel **3'** was also discussed.

From the practical standpoint, it is advisable to use acetone, methanol, or acetonitrile and their mixtures with water as solvents for raising the selectivity of oxidation of organic compounds by hydrogen peroxide on TS-1.

CONCLUSIONS

(1) Kinetic parameters of H_2O_2 decomposition in methanol, propanol-1, propanol-2, acetonitrile, and acetone and the selectivity of formation of molecular oxygen on TS-1 catalyst at 30–35°C were determined. The selectivity of O_2 formation grows with the substrate reactivity decreasing in the order propanol-2 > propanol-1 > acetone > acetonitrile ≥ methanol and with increasing concentration of water.

(2) It was shown that it is advisable to use acetone, acetonitrile, methanol, and their aqueous solutions as selective solvents for oxidation of organic compounds with hydrogen peroxide on TS-1.

REFERENCES

1. Notari, B., *Adv. Catal.*, 1996, vol. 41, pp. 253–334.
2. Perego, C., Carati, A., Ingallina, P., et al., *Appl. Catal. A, General*, 2001, vol. 221, pp. 63–72.
3. Bellussi, G., Carati, A., Clerici, M.G., et al., *J. Catal.,*

1992, vol. 133, pp. 220–230.

4. Kholdeeva, O.A. and Trukhan, N.N., *Uspekhi Khim*., 2006, vol. 75, no. 5, pp. 460–481.
5. US Patent 5683 952.
6. Kumar, R. and Bhaumik, A., *Micropor. Mesopor. Mater*., 1998, vol. 21, pp. 497–504.
7. Clerici, M.G., Bellussi, G., and Romano, U.*, J. Catal*., 1991, vol. 129, pp. 159–167.
8. Hong Liu, Guanzhong Lu, Yanglong Guo, et al., *Chem. Eng. J*., 2006, vol. 116, pp. 179–186.
9. Maspero, F. and Romano, U.*, J. Catal.,* 1994, vol. 146, pp. 476–482.
10. Bonino, F., Damin, A., and Ricchiardi, G., *J. Phys. Chem. B*, 2004, vol. 108, pp. 3573–3583.
11. Gang Li, Xiangsheng Wang, Xinwen Guo, et al., *Mater. Chem. Phys*., 2001, vol. 71, pp. 195–201.
12. Huybrechts, D.R.C., De Brycker, L., and Jacods, P.A., *Nature*, 1990, vol. 345, pp. 240–247.
13. Masahiro Fujiwara, Qiang Xu, Yoshie Souma, et al., *J. Mol. Catal. A, Chem*., 1999, vol. 142, pp. 77–86.