

The Influence of Organic Additives on the Regioselectivity of Oxygenation of Alkanes with Hydrogen Peroxide in the Presence of TS-1 Titanium Silicalite

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Abstract—Hydrogen peroxide oxidizes *n*-hexane, *n*-heptane, and *n*-octane at 50°C in the presence titanium silicalite TS-1 as a catalyst, forming isomeric mixtures of ketones and alcohols. Admixtures of organic acids, alcohols, benzene, and ethylbenzene sharply change the ratio of position isomers. For example, the normalized ratio is C(4) : C(3) : C(2) = 0.44 : 1.0 : 0.47 for *n*-heptane oxidation in the absence of additives, but it becomes 0.52 : 1.0 : 1.00 in the presence of benzyl alcohol and the addition of ethylbenzene changes it to 0.16 : 1.0 : 0.94.

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The problem of enhancement of selectivity is very important in the catalytic functionalization of saturated hydrocarbons [1–10], since only one particular product is usually of practical value in chemical processes. Homogeneous and heterogeneous catalytic systems based on transition metal compounds [11–14], in particular, a titanium derivative [15–17], have been developed in recent years for the oxidation of organic substances. It is known that microporous titanium silicalite TS-1 catalyzes the oxidation of hydrocarbons including alkanes, with hydrogen peroxide [18–24]. Recently, we have shown [25] that the oxidation of linear alkanes proceeds with a high degree of regioselectivity; e.g., in the oxidation of *n*-heptane, the methylene groups in the 3-position of the hydrocarbon chain display a 2.5 times higher reactivity than other methylene groups. Methyl groups are not oxidized at all.

In this paper, we report the first results obtained in the study of the effect of various additives on the yield of products and regioselectivity in the TS-1-catalyzed solvent-free oxidation of higher saturated hydrocarbons with hydrogen peroxide.

EXPERIMENTAL

Titanium silicalite TS-1 was obtained by hydrothermal crystallization of a gel containing silicon, titanium, and a tetrapropylammonium salt according to a procedure described earlier [23]. The Si/Ti ratio was determined by means of spectral techniques and was equal to 20. The surface area measured by the gas adsorption technique (BET) was ~373 m²/g. Hydrogen peroxide was used in the form of 35% aqueous solution (Fluka).

Oxidation of alkanes was carried out in a cylindrical glass vessel with a jacket through which water from a thermostat was circulated. Usually, 0.05 ml of alkane, 0.2 ml of hydrogen peroxide, and 0.05 ml of an organic substance were used in the reaction. Other reaction conditions are presented in the captions to the tables. After cooling, a certain amount of acetonitrile containing nitromethane was added to the reaction mixture as an internal standard; solid TS-1 was filtered off. The sampled reaction solution was analyzed by means of the GLC technique both before and after the treatment (for 10–20 min) of the solution with an excess of solid triphenylphosphine. This method that we proposed for determining not only the corresponding respective ketone and alcohol, but also alkyl hydroperoxide is described in [3, 9, 26–35].

The GLC analysis was performed with a 3700 chromatograph on a capillary column coated with FFAP/OV-101 at a 20/80 ratio by mass, 30 m × 0.2 mm × 0.3 μm; helium as a carrier gas. Chromatograms were preliminarily calibrated using authentic samples of the alkane oxidation products.

RESULTS AND DISCUSSION

We have studied the oxidation of three linear alkanes (normal hexane, heptane, and octane) with hydrogen peroxide catalyzed by titanium silicalite TS-1 in the absence of a solvent (except for water that is present in 35% hydrogen peroxide). All the results obtained including the influence of various additives on the regioselectivity in the oxidation of normal hexane, heptane, and octane are collated in Tables 1–3. The

Table 1. Oxidation of *n*-hexane with hydrogen peroxide catalyzed by TS-1^a

Additive	Total products, μmol	Product composition, wt %				Relative selectivity ^b	
		one-3	one-2	ol-3	ol-2	3	2
None	2.0	0	0	71.8	28.2	1.0	0.39
CH ₃ COOH	2.5	0	0	72.3	27.7	1.0	0.38
(CH ₃) ₂ CHCOOH	1.9	0	0	56.2	43.8	1.0	0.88
PhCOOH	2.5	0	0	60.4	39.6	1.0	0.66
PhCH ₂ OH	1.8	0	0	28.6	71.4	1.0	2.50

^a Reaction conditions: 30 min, 50°C, 5 mg of TS-1.^b The ratio of the total quantity of all oxygenates in the 2-position to the total quantity of oxygenates in the 3-position.**Table 2.** Oxidation of *n*-heptane with hydrogen peroxide catalyzed by TS-1^a

Additive	Total products, μmol	Product composition, wt %						Relative selectivity ^b		
		one-4	one-3	one-2	ol-4	ol-3	ol-2	4	3	2
None	4.6	2.3	20.5	20.0	10.9	38.4	7.3	0.44	1.0	0.47
None ^c	2.5	0.7	6.7	6.0	11.1	53.3	22.3	0.40	1.0	0.58
CH ₃ COOH	1.6	0.91	4.01	2.9	8.3	52.2	11.8	0.28	1.0	0.37
CH ₃ CH ₂ COOH	1.0	1.6	11.5	9.7	10.9	49.7	16.6	0.41	1.0	0.42
(CH ₃) ₂ CHCOOH	5.5	0.6	6.8	6.1	12.9	54.9	18.7	0.43	1.0	0.40
PhCOOH	1.3	3.1	3.4	13.0	9.3	52.0	19.2	0.45	1.0	0.58
<i>c</i> -C ₆ H ₁₁ COOH	3.5	0.6	3.9	8.5	6.2	59.6	21.3	0.19	1.0	0.50
PhCH ₂ OH	1.3	0.7	2.3	10.9	10.3	42.6	33.2	0.52	1.0	1.00
<i>c</i> -C ₆ H ₁₁ CH ₂ OH	8.9	0.7	6.2	1.1	13.2	58.9	19.9	0.42	1.0	0.42
PhH	2.4	3.5	5.3	12.6	8.5	33.1	37.2	0.62	1.0	1.30
PhCH ₂ CH ₃	2.3	0	10.4	6.0	8.8	38.0	36.8	0.16	1.0	0.94

^a Reaction conditions: 30 min, 50°C, 5 mg of TS-1.^b Normalized ratios of the quantity of all oxygenates in the 2- and 4-positions to the total quantity of all oxygenates in the 3-position.^c Instead of aqueous solutions of hydrogen peroxide, its adduct with urea was used.**Table 3.** Oxidation of *n*-octane with hydrogen peroxide catalyzed by TS-1^a

Additive	Total products, μmol	Product composition, wt %						Relative selectivity ^b		
		one-4	one-3	one-2	ol-4	ol-3	ol-2	4	3	2
None	0.7	5.8	10.2	28.7	13.5	17.7	27.1	0.30	1.0	2.24
CH ₃ COOH	1.0	5.4	7.4	17.0	12.9	30.7	26.5	0.48	1.0	1.14
(CH ₃) ₂ CHCOOH	2.2	2.6	4.6	8.3	27.4	29.4	27.7	1.00	1.0	1.05
<i>c</i> -C ₆ H ₁₁ COOH	3.5	1.9	3.1	10.5	23.8	27.6	33.1	0.84	1.0	1.53
PhCH ₂ OH	1.6	2.8	5.2	15.7	20.6	26.2	29.6	0.75	1.0	1.60

^a Reaction conditions: 30 min, 50°C, 5 mg of TS-1.^b The ratio of the quantity of all oxygenates in the 2-4-position to the total quantity of all oxygenates in the 3-position.

product yields (total ketones and alcohols) in micromoles; the percentage distribution of the products; and, as the main result of this work, the parameters of the relative reactivity of various methylene groups with respect to the reactivity of hydrogen atoms in the 3-position of the hydrocarbon chains (taken as unit activity) are presented in the tables. In the case of oxidation of *n*-heptane, the parameters are normalized; i.e., it was taken into account that there is only one methylene group in the 4-position while positions 2 and 3 contain two CH₂ groups each. Note that the products of oxidation at the methyl groups were not found. Comparison of the chromatograms of the samples obtained before and after their reduction with solid triphenylphosphine [3, 9, 26–35] showed that corresponding alkyl hydroperoxides are not present in the reaction mixture in substantial quantities; ketones and alcohols are the products of the reaction.

In the case of *n*-hexane (Table 1) in the absence of additives, oxidation proceeds with substantial prevalence of oxygenates in the 3-position: the ratio C(3) : C(2) for the ketone + alcohol yield is 1.0 : 0.39. Acetic acid does not change the C(3) : C(2) ratio. Other acids cause some decrease in this ratio, although they increase the yield of the products a little. Isobutyric and benzoic acids level the reactivity of the methylene groups in the 2- and 3-positions. At the same time, the addition of benzyl alcohol results in a dramatic change in selectivity, C(3) : C(2) = 1.0 : 2.50 in this case; i.e., there is substantial prevalence of the products of oxidation in the 2-position already.

The oxidation of *n*-heptane (Table 2) in the absence of additives prevalently yields oxygenates in the 3-position (the normalized quantity of oxygenates in the 3-position is more than two times that of other isomers). In the case of addition of aliphatic (acetic, propionic, isobutyric) acids, this prevalence becomes even more pronounced. At the same time, as in the case of hexane, the addition of benzyl alcohol results in an increase in the proportion of 4- and 2-isomers; thus, the reactivities of positions 3 and 2 appear to be equal. It is interesting that the addition of benzene leads to an increase in the proportion of 4- and 2-isomers, and the quantity of oxygenates in the 2-position is 1.3 times the sum of the oxidation products in the 3-position. The addition of ethylbenzene leads to a substantial reduction in the amount of the 4-isomers (its amount is 6.25 times below that of the 3-isomers) while the amount of 2-isomers increases and is almost equal to that of the 3-isomers.

All the test additives (some aliphatic acids and benzyl alcohol) noticeably reduce the relative amount of the 2-isomers and increase the concentration of 4-isomers in the oxidation of *n*-octane (Table 3).

Thus, the results of this work show that it is possible to achieve a significant change in the regioselectivity in oxidation of alkanes on TS-1 by the addition of various organic compounds to the reaction mixture, and the

direction of the change completely depends on the nature of the admixed compound.

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REFERENCES

1. E. I. Bagrii and A. I. Nekhaev, Zh. Vses. Khim. O-va im. D. I. Mendeleeva **34**, 634 (1989).
2. A. E. Shilov and G. B. Shul'pin, Chem. Rev. **97**, 2879 (1997).
3. A. E. Shilov and G. B. Shul'pin, in *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes* (Kluwer Academic, Dordrecht, 2000), Chap. X.
4. M. V. Avdeev, E. I. Bagrii, G. B. Maravin, et al., Pet. Chem. **40**, 391 (2000).
5. G. B. Maravin, M. V. Avdeev, and E. I. Bagrii, Neftekhimiya **40**, 3 (2000) [Pet. Chem. **40**, 1 (2000)].
6. A. I. Nekhaev, R. S. Borisov, V. G. Zaikin, and E. I. Bagrii, Pet. Chem. **42**, 418 (2002).
7. A. I. Nekhaev, R. S. Borisov, V. G. Zaikin, and E. I. Bagrii, Pet. Chem. **42**, 238 (2002).
8. M. V. Avdeev, E. I. Bagrii, G. B. Maravin, and Yu. M. Korablev, Kinet. Catal. **43**, 38 (2002).
9. G. B. Shul'pin, C. R. Acad. Sci., Chim. **6**, 163 (2003).
10. G. B. Shul'pin, in *Transition Metals for Organic Synthesis*, Ed. by M. Beller and C. Bolm (Wiley-VCH, Weinheim, 2004), Vol. 2, p. 215.
11. D. R. Corbin and N. Herron, J. Mol. Catal. **86**, 343 (1994).
12. J. M. Thomas, Angew. Chem., Int. Ed. Engl. **38**, 3588 (1999).
13. J. M. Thomas and R. Raja, Chem. Commun., 675 (2001).
14. K. S. Suslick, P. Bhyrappa, J.-H. Chou, et al., Acc. Chem. Res. **38**, 283 (2005).
15. O. A. Kholdeeva and N. N. Trukhan, Usp. Khim. **75**, 460 (2006).
16. O. A. Kholdeeva, Top. Catal. **40**, 229 (2006).
17. O. A. Kholdeeva, M. S. Mel'gunov, A. N. Shmakov, et al., Catal. Today **91–92**, 205.
18. C. B. Khouw, C. B. Darrt, J. A. Labinger, and M. E. Davis, J. Catal. **149**, 195 (1994).
19. P. J. Kooyman, G. C. A. Luijkx, A. Arafat, and H. Van Bekkum, J. Mol. Catal. A: Chem. **111**, 167 (1996).
20. I. Vankelecom, K. Verduyck, N. Moens, et al., Chem. Commun., 137 (1997).
21. M. G. Clerici, Top. Catal. **15**, 257 (2001).
22. R. H. P. R. Poladi and C. C. Landry, Micropor. Mesopor. Mater., **52**, 11 (2002).

23. T. Sooknoi and J. Limtrakul, *Appl. Catal., A* **233**, 227 (2002).
24. I. Halasz, M. Agarwal, E. Senderov, and B. Markus, *Appl. Catal., A* **241**, 167 (2003).
25. G. B. Shul'pin, T. Sooknoi, V. B. Romakh, et al., *Tetrahedron Lett.* **47**, 3071 (2006).
26. G. B. Shul'pin, *J. Mol. Catal., A: Chem.* **189**, 39 (2002).
27. G. B. Shul'pin and A. N. Druzhinina, *React. Kinet. Catal. Lett.* **47**, 207 (1992).
28. G. B. Shul'pin and G. V. Nizova, *React. Kinet. Catal. Lett.* **48**, 333 (1992).
29. G. B. Shul'pin, D. Attanasio, and L. Suber, *J. Catal.* **142**, 147 (1993).
30. G. B. Shul'pin, M. M. Bochkova, and G. V. Nizova, *J. Chem. Soc., Perkin Trans. 2*, 1465 (1995).
31. G. B. Shul'pin, G. V. Nizova, and Y. N. Kozlov, *New J. Chem.* **20**, 1243 (1996).
32. G. B. Shul'pin, Y. N. Kozlov, G. V. Nizova, et al., *J. Chem. Soc., Perkin Trans. 2*, 1351 (2001).
33. G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, et al., *Adv. Synth. Catal.* **346**, 317 (2004).
34. L. S. Shul'pina, A. R. Kudinov, G. Süß-Fink, et al., *Pet. Chem.* **45**, 336 (2005).
35. M. J. D. M. Jannini, L. S. Shul'pina, U. Schuchardt, and G. B. Shul'pin, *Pet. Chem.* **45**, 413 (2005).