Conference Paper

Mechanism of Allyl Alcohol Epoxidation with Hydrogen Peroxide at Titanium Catalyst (Ts-1)

Zh Yu Pastukhova, L G Bruk, and V R Flid

Institute of Fine Chemical Technology, Moscow Technological University, 86 Avenue Vernadskogo, Moscow, 119571, Russia

Abstract

Allyl alcohol epoxidation mechanism at the titanosilicate was studied. The best results were obtained for the hypothesis involving the hydrogen peroxide and allyl alcohol adsorption at the active catalyst centres with subsequent interaction of the surface intermediates with each other, with the formation of glycidol adsorbed on the active centre, free catalyst centre and molecule of water.

Corresponding Author:
Zh Yu Pastukhova
pastuhowa.zhanna@yandex.ru

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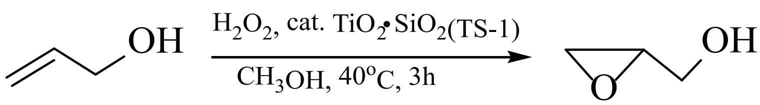
1. Scope

Oxygen-containing heterocyclic compounds (oxides olefins, cyclic acetals, etc.) are important products and intermediates of the basic and fine organic synthesis. Great practical interest is the glycidol oxide of allyl alcohol. It is a valuable intermediate product in the manufacture of surfactants, plasticizers, textile dyes, drugs, pesticides, some rubbers, paints, thermosetting resins and other [1].

2. Results and discussion

There are several basic methods for producing glycidol such as epoxidation of allyl alcohol with organic hydroperoxides at vanadium inorganic compounds as a catalysis; glycerol carbonate decomposition; chlorohydrins method; oxidation method; epoxidation of allyl alcohol with hydrogen peroxide [2].

One of the most promising methods for producing glycidol is the epoxidation of allyl alcohol by hydrogen peroxide on the titanium-containing catalyst.



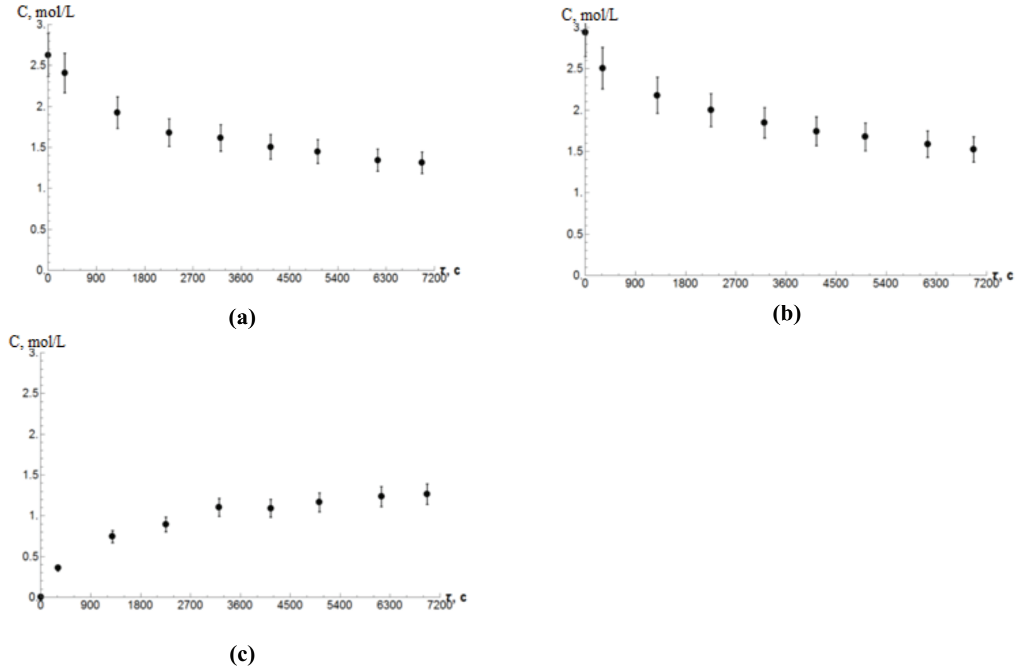


Figure 1: The concentrations of allyl alcohol (a), hydrogen peroxide (b) and glycidol (c) in the course of a typical kinetic experiment.

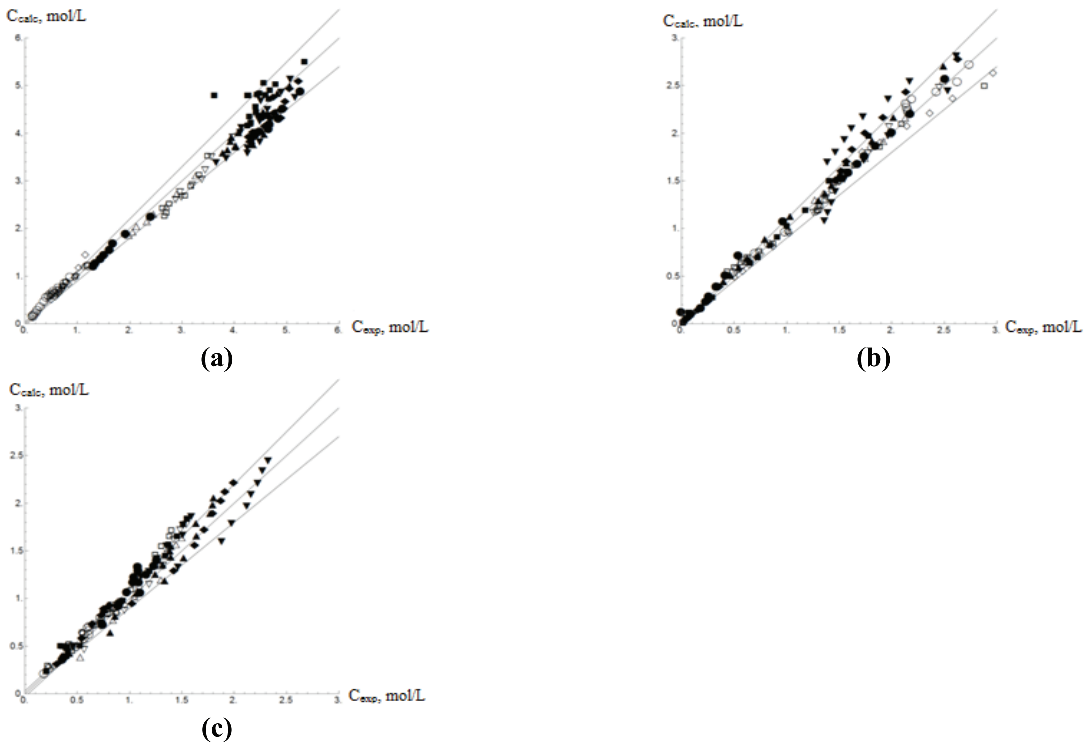


Figure 2: The accordance between calculated and experimental concentrations of allyl alcohol (a), hydrogen peroxide (b) and glycidol (c) for all experiments (mechanism 14, table 1).

It was studied the epoxidation mechanism of allyl alcohol using titanosilicate zeolite (ts-1) at 40°C by means of procedures for the nomination and discrimination of mechanism hypotheses. The hypotheses were advanced on the basis of literature data and

Table 1: Hypothetical mechanisms for the allyl alcohol epoxidation.

Mechanism 1	Mechanism 2	Mechanism 3
1 $X_0+H_2O_2 \rightleftarrows X_1$ 2 $X_1 + C_3H_6O \rightarrow C_3H_6O_2 + H_2O + X_0$	1 $X_0 + C_3H_6O \rightleftarrows X_2$ 2 $X_1 + H_2O_2 \rightarrow C_3H_6O_2 + H_2O + X_0$	1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_0 + C_3H_6O \rightleftarrows X_2$ 3 $X_1 + C_3H_6O \rightarrow C_3H_6O_2 + H_2O + X_0$ 4 $X_1 + H_2O_2 \rightarrow C_3H_6O_2 + H_2O + X_0$
Mechanism 4	Mechanism 5	Mechanism 6
1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_1 + C_3H_6O \rightleftarrows X_3$ 3 $X_3 \rightarrow C_3H_6O_2 + H_2O + X_0$	1 $X_0 + C_3H_6O \rightleftarrows X_2$ 2 $X_2 + H_2O_2 \rightleftarrows X_3$ 3 $X_3 \rightarrow C_3H_6O_2 + H_2O + X_0$	1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_0 + C_3H_6O \rightleftarrows X_2$ 3 $X_1 + C_3H_6O \rightleftarrows X_3$ 4 $X_2 + H_2O_2 \rightleftarrows X_3$ 5 $X_3 \rightarrow C_3H_6O_2 + H_2O + X_0$
Mechanism 7	Mechanism 8	Mechanism 9
1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_0 + C_3H_6O \rightleftarrows X_2$ 3 $X_1 + X_2 \rightarrow C_3H_6O_2 + H_2O + 2X_0$	1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_1 + C_3H_6O \rightarrow H_2O + X_4$ 3 $X_4 \rightleftarrows C_3H_6O_2 + X_0$	1 $X_0 + C_3H_6O \rightleftarrows X_2$ 2 $X_1 + H_2O_2 \rightarrow H_2O + X_4$ 3 $X_4 \rightleftarrows C_3H_6O_2 + X_0$
Mechanism 10	Mechanism 11	Mechanism 12
1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_0 + C_3H_6O \rightleftarrows X_2$ 3 $X_1 + C_3H_6O \rightarrow H_2O + X_4$ 4 $X_2 + H_2O_2 \rightarrow H_2O + X_4$ 5 $X_4 \rightleftarrows C_3H_6O_2 + X_0$	1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_1 + C_3H_6O \rightleftarrows X_3$ 3 $X_3 \rightarrow H_2O + X_4$ 4 $X_4 \rightleftarrows C_3H_6O_2 + X_0$	1 $X_0 + C_3H_6O \rightleftarrows X_2$ 2 $X_2 + H_2O_2 \rightleftarrows X_3$ 3 $X_3 \rightarrow H_2O + X_4$ 4 $X_4 \rightleftarrows C_3H_6O_2 + X_0$
Mechanism 13	**Mechanism 14**	
1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_0 + C_3H_6O \rightleftarrows X_2$ 3 $X_1 + C_3H_6O \rightleftarrows X_3$ 4 $X_2 + H_2O_2 \rightleftarrows X_3$ 5 $X_3 \rightarrow H_2O + X_4$ 6 $X_4 \rightleftarrows C_3H_6O_2 + X_0$	1 $X_0 + H_2O_2 \rightleftarrows X_1$ 2 $X_0 + C_3H_6O \rightleftarrows X_2$ 3 $X_1 + X_2 \rightarrow X_4 + H_2O + X_0$ 4 $X_4 \rightleftarrows C_3H_6O_2 + X_0$	*C_3H_6O – allyl alcohol; $C_3H_6O_2$ – glycidol; X_0 – the catalyst active centre; $X_1 \equiv X_0 \cdot H_2O_2$; $X_2 \equiv X_0 \cdot C_3H_6O$, $X_3 \equiv X_0 \cdot H_2O_2 \cdot C_3H_6O$; $X_4 \equiv X_0 \cdot C_3H_6O_2$.

the preliminary experiment results (table 1). Discrimination hypothetical mechanisms were carried out on the basis of the kinetic experiment results with varying concentrations of allyl alcohol, hydrogen peroxide and glycidol (Figure 1).

For each hypothesis, it was formulated the corresponding system of differential equations and carried out the estimation of the rate constants. The quality of the experimental data description was judged by the residual sums of squared deviations and correlation coefficients. The most probable mechanism (14, table 1) involves the hydrogen peroxide and allyl alcohol adsorption at the catalyst active centers and the glycidol formation as adsorbed molecules of the reactants interaction via the reversible step.

3. Conclusions

The best description of the results are obtained for the hypothesis involving the hydrogen peroxide and allyl alcohol adsorption at the two active catalyst centres with subsequent interaction of the surface intermediates with each other, with the formation of glycidol adsorbed on the active centre, free catalyst centre and molecule of water.

Acknowledgments

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References

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