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KINETIC INVESTIGATION OF THE CATALYTIC DECOMPOSITION OF ORGANIC PEROXIDES BY PULSE CHROMATOGRAPHY

A. F. SHUSHUNOVA

Department of Chemistry and Chemistry Institute, N. I. Lobachevsky State University, Gagarin Avenue 23, Block 5, 603022 Gorky (U.S.S.R.)

SUMMARY

The kinetics of the catalytic transformation of cumyl and *tert.*-butyl hydroperoxides under gas chromatographic column conditions has been studied. Amphoteric and acidic metal oxides were used as the catalysts. The rate constants of the reactions and half-lives of the hydroperoxides studied have been calculated. The catalysts used can be arranged in order of decreasing catalytic activity: $V_2O_5 > Co_2O_3 > Fe_2O_3 > Al_2O_3$, ZnO. The kinetic curves for the hydroperoxide consumption and the accumulation of the main products of their catalytic decomposition have been obtained.

INTRODUCTION

Gas chromatography (GC) has been widely used in this laboratory to study the kinetics of chemical reactions of hydroperoxides[1,2]. However, analytical GC cannot be used with fast reactions, because by the time a sample has been taken from the reaction mixture and subsequently analysed the chemical process being studied has progressed further.

New possibilities of studying the kinetics of chemical reactions have been provided by the so-called pulse chromatographic methods in which both the chemical reaction and the analysis are combined into a single process[3–8].

In the present work on the kinetics of catalytic transformations of cumyl and *tert.*-butyl hydroperoxides under GC column conditions a modified pulse method has been applied.

EXPERIMENTAL AND RESULTS

Part of the packed chromatographic column was inserted into the evaporator and operated as a microreactor and the remainder operated as a separating column. The hydroperoxide solution was introduced directly into the microreactor with a microsyringe in the absence of carrier gas flow. The sample was kept inside the microreactor from 0.5 to 30 min, then a carrier gas flow was passed and the sample was transported into the separation part of the column. A blank test with no catalyst was

performed. The catalysts used were amphoteric and acidic metal oxides, Fe_2O_3, Co_2O_3, Al_2O_3, ZnO, V_2O_5, which were introduced directly into the sorbent in the microreactor using various methods. The catalyst mass introduced was $0.3 \cdot 10^{-3}$ g V_2O_5, and $3.0 \cdot 10^{-3}$ of the other oxides. After six to eight packings the microreactor contents were replaced. The temperatures in the microreactor and the separating column were constant.

A Tsvet-104 gas chromatograph equipped with a flame ionization detector was employed. As a solvent for hydroperoxides, chlorobenzene applied, which was purified by the usual method. The chromatographic conditions for *tert.*-butyl hydroperoxide were as follows: glass column (110 cm × 0.3 cm), sorbent Celite 545–20% dinonyl phthalate; carrier gas (helium) flow-rate 60 ml/min; dose 1 μl; temperature of column thermostat 50°C. The chromatographic conditions for cumyl hydroperoxide were: glass column (37 cm × 0.3 cm), sorbent Celite 545–5% polyethylene glycol adipate–3% dinonyl phthalate; carrier gas (helium) flow-rate 200 ml/min; temperature of column thermostat 80°C; dose 0.2 μl.

Figs. 1 and 2 present chromatograms of the catalytic decomposition of cumyl and *tert.*-butyl hydroperoxides in the presence of the heterogeneous oxidizing catalysts Fe_2O_3, Co_2O_3, V_2O_5. From the results of the chromatographic analysis, the kinetic curves for hydroperoxide consumption and accumulation of the main products of their catalytic decomposition under GC column conditions have been obtained, Figs. 3 and 4. The main products of catalytic decomposition of *tert.*-butyl hydroperoxide are acetone and *tert.*-butanol:
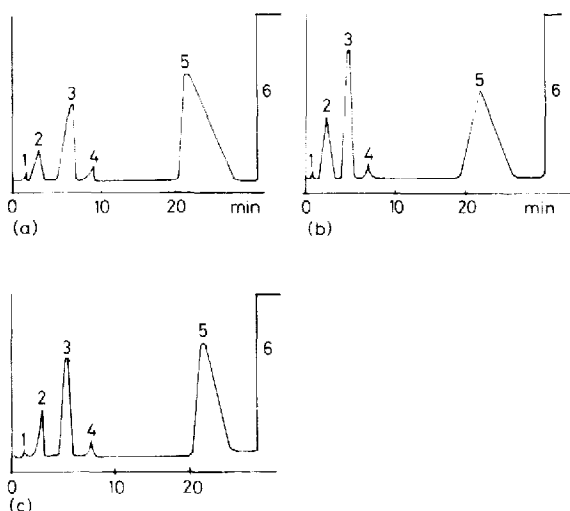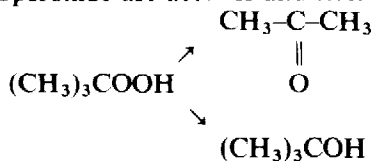
$$\text{(CH}_3\text{)}_3\text{COOH} \quad \overset{\nearrow}{\underset{\searrow}{}} \quad \begin{matrix} \text{CH}_3\text{--C--CH}_3 \\ \| \\ \text{O} \end{matrix} \\ \text{(CH}_3\text{)}_3\text{COH}$$

Fig. 1. Chromatograms of the catalytic decomposition of *tert.*-butyl hydroperoxide under GC column conditions. Catalysts: (a) V_2O_5; (b) Fe_2O_3; (c) Co_2O_3. The temperature in the microreactor was 50°C. Peaks: 1 = methanol; 2 = acetone; 3 = *tert.*-butanol; 4 = *tert.*-butyl peroxide; 5 = *tert.*-butyl hydroperoxide; 6 = chlorobenzene solvent.
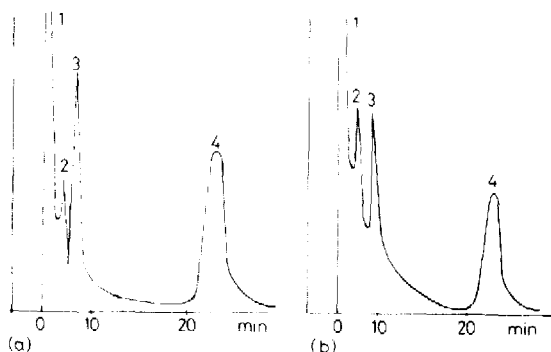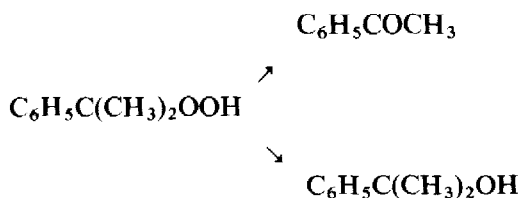
Fig. 2. Chromatograms of the catalytic decomposition of cumyl hydroperoxide under GC column conditions. Catalysts: (a) Co_2O_3; (b) Fe_2O_3. Peaks: 1 = chlorobenzene solvent; 2 = acetophenone; 3 = 2-phenyl-2-propanol; 4 = cumyl hydroperoxide.

The main decomposition products of cumyl hydroperoxide, catalyzed by Fe_2O_3, Co_2O_3, are acetophenone and 2-phenyl-2-propanol

$$C_6H_5COCH_3$$

$$\nearrow$$

$$C_6H_5C(CH_3)_2OOH$$

$$\searrow$$

$$C_6H_5C(CH_3)_2OH$$
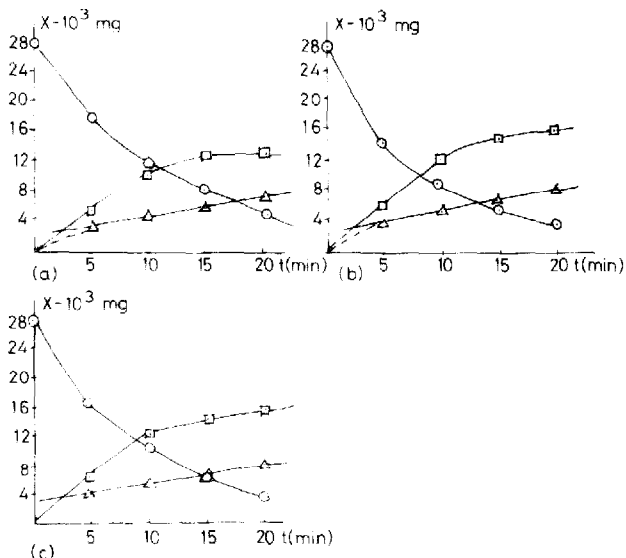
i.e., homolytic decomposition occurs.

Fig. 3. Kinetic curves for *tert.*-butyl hydroperoxide consumption and accumulation of its main catalytic decomposition products in the chromatographic regime. ⊙—⊙, Amount of *tert.*-butyl hydroperoxide; ☐—☐, amount of *tert.*-butanol, △—△, amount of acetone. Catalysts: (a) V_2O_5; (b) Fe_2O_3; (c) Co_2O_3.
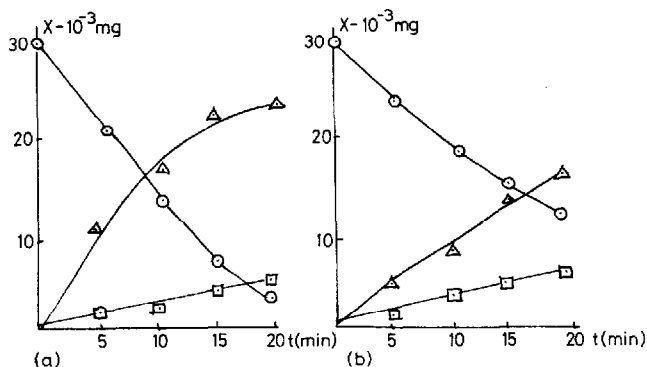
Fig. 4. Kinetic curves for cumyl hydroperoxide consumption and the accumulation of its main catalytic decomposition products under GC column conditions. ⊙—⊙, Amount of cumyl hydroperoxide; △—△, amount of 2-phenyl-2-propanol; ⊡—⊡, amount of acetophenone. Catalysts: (a) Co_2O_3; (b) Fe_2O_3.

The amphoteric oxides Al_2O_3 and ZnO are catalytically inactive and do not catalyze the decomposition of cumyl hydroperoxide.

From the results of the chromatographic analysis, the activity of the catalysts used in the present work decreases in the following order: $V_2O_5 > Co_2O_3 > Fe_2O_3 > Al_2O_3$, ZnO.
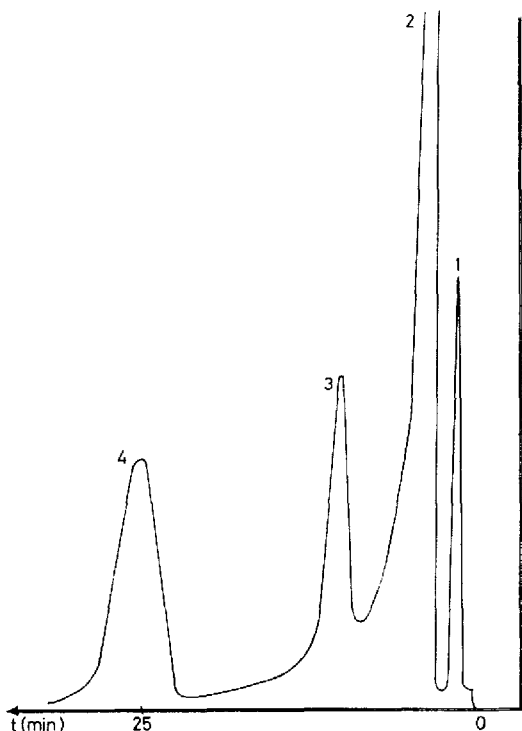

Fig. 5. Chromatogram of the catalytic decomposition of cumyl hydroperoxide under GC column conditions. Catalyst: KU-2 ion exchanger. Peaks: 1 = acetone; 2 = chlorobenzene; 3 = phenol; 4 = cumyl hydroperoxide.

TABLE I

KINETIC CHARACTERISTICS OF THE CATALYTIC DECOMPOSITION OF *tert.*-BUTYL HYDROPEROXIDE UNDER GC COLUMN CONDITIONS

Concentration of hydroperoxide: $0.1\ M\ 27.0 \cdot 10^{-3}$ mg in sample. The relative error of the mean value (from three measurements) is 7%.

Catalyst	$kK \cdot 10^4$ (s^{-1})	$K \cdot 10^{-3}$	$k \cdot 10^7$ (s^{-1})	$\tau_{\frac{1}{2}} \cdot 10^2$ (s)
V_2O_5	11.5	1.582	7.27	0.16
Fe_2O_3	19.93	1.582	12.60	0.09
Co_2O_3	18.40	1.582	11.63	0.10

The ionic decomposition of cumyl hydroperoxide under GC column conditions was catalyzed by the ion exchanger KU-2 ($3.0 \cdot 10^{-3}$ g), which is relating to the polystyrene sulphocationites. In this case the main decomposition products are phenol and acetone (Fig. 5).

It has been established previously[7,8] that the decomposition reactions of *tert.*-butyl and cumyl hydroperoxide in the liquid phase were first order, and the rate of catalytic decomposition of the hydroperoxides could be expressed by the equation

$$\frac{dx}{dt} = kKX; \qquad \log \frac{X_0}{X} = \frac{kK}{2.303} \cdot t$$

where X is the amount of substance available at time t, k is the true rate constants of the reaction, K is the partition coefficient, X_0 is the initial amount of substance and $Kk = K_{eff}$ is the effective rate constant of the reaction.

Having determined the partition coefficient, K, chromatographically, the true rate constant of the reaction in a liquid phase can be calculated:

$$k = \frac{2.303\ tg\ \alpha}{K}$$

TABLE II

KINETIC CHARACTERISTICS OF THE CATALYTIC DECOMPOSITION OF CUMYL HYDROPEROXIDE UNDER GC COLUMN CONDITIONS

Concentration of hydroperoxide: $1\ M\ 29.7 \cdot 10^{-3}$ mg in sample. The relative error of the mean value (from three measurements) is 7%.

Catalyst	$kK \cdot 10^4$ (s^{-1})	$K \cdot 10^{-3}$	$k \cdot 10^7$ (s^{-1})	$\tau_{\frac{1}{2}} \cdot 10^{-2}$ (s)
V_2O_5	15.4	3.89	3.95	0.2
Fe_2O_3	9.20	3.89	2.36	0.2
Co_2O_3	7.09	3.89	1.82	—

The half-life of hydroperoxides was calculated by the equation:

$$\tau_{\frac{1}{2}} = 2.303 \log 2 \cdot \frac{1}{kK} = \frac{0.69}{kK}$$

The kinetic characteristics of the catalytic decomposition of cumyl and *tert.*-butyl hydroperoxides are given in Tables I and II.

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