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Abstract

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THE ROLE OF THE SURFACE IN THE CHAIN-PROPAGATION REACTION DURING THE LIQUID-PHASE OXIDATION OF *n*-BUTANE

According to modern concepts of the mechanism of liquid-phase oxidation of hydrocarbons, these processes are slow chain reactions in which the active particles carrying out the chain process are peroxy radicals $\mathrm{R\dot{O}_2}$ (^{1}). The primary intermediate product of liquid-phase oxidation of hydrocarbons is found to be the corresponding hydroperoxides, formed by the reaction:

$$\mathrm{R\dot{O}_2} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\cdot}. \qquad (1)$$

The process of oxidation of *n*-butane in the liquefied state at temperatures and pressures close to the critical values, proposed by one of us (^{2}), differs somewhat in the composition of the observed products from the oxidation processes of higher homologues of the paraffin series, for example *n*-decane (^{3}). Along with compounds formed from hydroperoxides, appreciable amounts of acetaldehyde, acetone, methyl and ethyl alcohols, methyl acetate, and ethyl acetate are detected in the oxidation of butane.

By analogy with the oxidation of hydrocarbons in the gas phase, it may be assumed that these compounds are products of isomerization and decomposition of the peroxy radical (^{4}), and that under the conditions in which the process of liquid-phase oxidation of butane is carried out there exists a second direction of the chain-propagation reaction

$$\mathrm{R\dot{O}_2} \rightarrow \mathrm{R'CHO} + \mathrm{R''O}^{\cdot}. \qquad (2)$$

The final composition of the oxidation products is determined by competition between reactions (1) and (2).

The ratio of the rates of these reactions during the oxidation of butane in the gas phase depends strongly on the nature of the surface of the reaction vessel:

Fig. 1

Figure 1: Fig. 1

in stainless-steel vessels the rates of decomposition of the radical $RO_2^{\cdot}$ prove to be considerably greater than in glass vessels (^{5}).

In the present work we have shown that the metal surface of the reactor exerts a substantial influence on the mechanism of the chain-propagation reaction also during the oxidation of butane in the liquid phase.

Liquid-phase oxidation of hydrocarbons proceeds under conditions of intensive stirring of the reaction mixture, favoring heterogeneous processes. Indeed, in a number of studies, for example (^{6,7}), a decrease in the induction period and an increase in the rate of liquid-phase oxidation of hydrocarbons were observed when the surface was increased by introducing into the vessel certain salts and oxides insoluble in the reaction liquid. No changes in the composition of the oxidation products under the influence of surface development were found in these studies. In the oxidation of cyclohexane in a steel reactor, about 30% of cyclohexanol is formed not from hydroperoxide,

and directly from the radical $RO_2^{\bullet}$ (8). This indicates the influence of the metal surface on the chain-propagation mechanism, since in glass reactors all the cyclohexanol is formed through the intermediate cyclohexyl hydroperoxide. However, these experiments say nothing about competition between reactions (1) and (2), since in both reactors the same products are formed (without rupture of the C —C bond).

Fig. 1. Kinetic curves for the accumulation of products of the liquid-phase oxidation of *n*-butane in a glass reactor. Temperature 145°, pressure 50 atm. 1 —hydroperoxide; 2 —methyl ethyl ketone; 3 —secondary butyl alcohol; 4 —acetic acid; 5 —hydroperoxide in a steel reactor (according to data from (9)).

Having data on the rates and composition of the products of liquid-phase oxidation of *n*-butane in a stainless-steel reactor (9), we carried out a series of experiments in reactors made of molybdenum glass and quartz.

Since maintaining butane in the liquid state at a temperature of 145° requires the use of elevated pressure, a glass reactor operating under a two-sided pressure was constructed, in which the reacting substances (butane and the products of its oxidation) nowhere came into contact with metal. The reaction products were analyzed by gas-liquid chromatography (10), using a katharometer and an ionization-flame detector.

The very first experiments showed that in the glass reactor large amounts of *n*-butyl hydroperoxide accumulate, exceeding by a factor of 10–15 the concentrations of hydroperoxides in the products of butane oxidation in the metal reactor. In addition to the hydroperoxide, products of its further conversion are

Fig. 2

Figure 2: Fig. 2

also formed—methyl ethyl ketone and secondary butyl alcohol—and at deeper stages of the process small amounts of acetic acid appear (Fig. 1).

The decomposition products of the secondary butyl peroxy radical (acetone, acetaldehyde, etc.) at the early stages of butane oxidation in the glass reactor were found in amounts whose sum did not exceed 1 mol.% of the butane that had reacted, whereas in the metal reactor they amount to ∼ 20 mol.% of the butane.

Fig. 2. Kinetic curves for the accumulation of products of the liquid-phase oxidation of *n*-butane in a stainless-steel reactor: without packing (numbers without primes), with metal packing (numbers with one prime), and with glass packing (numbers with two primes). Temperature 145°, pressure 50 atm.
1, 1′, 1″ —acetaldehyde; 2, 2′, 2″ —acetone; 3, 3′, 3″ —ethyl alcohol; 4, 4′, 4″ —methyl ethyl ketone.

Table 1

Oxidation of *n*-butane in a steel reactor: temperature 145°, pressure 50 atm, degree of oxidation 5.5 mol. % butane

Reaction product	% of reacted butane, without packing	% of reacted butane, stainless-steel turnings	Rate of product accumulation, mol/l • h, without packing	Rate of product accumulation, mol/l • h, stainless-steel turnings
Acetaldehyde	3.1	4.7	0.010	0.040
Acetone	3.6	9.4	0.011	0.043
Ethyl alcohol	12.6	18.6	0.048	0.120
Methyl ethyl ketone	66.8	57.5	0.120	0.190
Acetic acid	10.0	6.2	0.320	0.650
Ethyl acetate	2.7	0.8	0.012	0.007
Methyl alcohol	1.2	2.8	–	–

Fig. 3

Figure 3: Fig. 3

Reaction product	% of reacted butane, without packing	% of reacted butane, stainless-steel turnings	Rate of product accumulation, mol/l · h, without packing	Rate of product accumulation, mol/l · h, stainless-steel turnings
Rate of butane consumption			0.331	0.629
$RO_2^\bullet + RH$	79.5	64.5		
Decomposition of $RO_2^\bullet$	20.5	35.5		

Comparing the kinetic curves in Fig. 1 with analogous curves for the oxidation of butane in a steel reactor (Fig. 2) (see also [9]), we see that the metallic surface of the reaction vessel, first, promotes isomerization and decomposition and, second, accelerates the consumption of hydroperoxides. This result was confirmed by experiments in a metal apparatus, the reactor of which was filled with stainless-steel turnings.

An increase in the metallic surface significantly increases the rates of accumulation of the products of decomposition of the radical $RO_2^\bullet$ in comparison with the process of butane oxidation in the same vessel without packing (Fig. 2). In vessels filled with stainless-steel turnings, the concentrations of acetaldehyde, acetone, ethyl and methyl alcohols increase strongly, while the concentrations of products formed from the hydroperoxide—methyl ethyl ketone, acetic acid (acetic acid is also obtained in part from acetaldehyde), and ethyl acetate—decrease (see Table 1).

Under the influence of the metal, there is also a decrease in the induction period and an increase in the overall oxidation rate, determined from the rate of butane consumption. At the same time, the rates of accumulation of the decomposition products of $RO_2^\bullet$ increase several times more than the rates of accumulation of the products of the hydroperoxide pathway. The acceleration of the reaction may be associated with an increase in the rate of chain branching due to an increase in the rate of hydroperoxide decomposition and the rate of acetaldehyde formation, which is converted into the extremely reactive acetyl hydroperoxide.

Fig. 3. Kinetic curves for the consumption of *n*-butyl hydroperoxide and the accumulation of products of its transformation during thermal decomposition of the hydroperoxide in an argon atmosphere in a steel vessel without packing

(numbers without primes) and with stainless-steel packing (primed numbers). Temperature 145°, pressure 50 atm. 1, 1′—consumption of hydroperoxide; 2, 2′—accumulation of methyl ethyl ketone; 3, 3′—accumulation of sec-butyl alcohol.

Similar experiments with the packing of the steel reactor with glass wool led only to a slight decrease in the rates of accumulation of all products of butane oxidation.

Since a metal surface promotes the decomposition of *n*-butyl hydroperoxide, it was necessary first of all to make sure that the observed change in the rates of accumulation of the products is not the result of a change in the rate and direction of decomposition of *n*-butyl hydroperoxide under the influence of the metal. For this purpose experiments were carried out in which *n*-butane, oxidized in a glass vessel and containing secondary butyl hydroperoxide, was transferred to a metal reactor (with and without packing), where the rates of consumption of the hydroperoxide and of accumulation of the products of its decomposition were measured in an argon atmosphere at the same temperatures (145°) and pressures (50 atm.) as those at which the butane-oxidation experiments were conducted.

It follows from Fig. 3 that the amount of decomposed hydroperoxide corresponds to the amount of methyl ethyl ketone and butyl alcohol formed; compounds containing fewer than 4 carbon atoms in their molecule are not formed during the decomposition of *n*-butyl hydroperoxide.

Consequently, the introduction of packing affects only the rate of consumption of *n*-butyl hydroperoxide and does not change at all the ratios among the individual products of its transformation.

The results obtained in the present work lead us to a conclusion that is very interesting from the standpoint of the theory of branched chain reactions: the isomerization and decomposition of the peroxide radical $RO_2\cdot$ in the liquid phase is a heterogeneous (catalytic) reaction. Indeed, if, when the process is carried out in a glass vessel, the decomposition products of $RO_2\cdot$ are not detected in any appreciable quantities, while in a steel reactor they amount to about 20 mol.% of the butane that has reacted, then it is evident that the decomposition reaction of $RO_2\cdot$ under these conditions (temperature 145°, pressure 50 atm.) proceeds almost exclusively on the metal surface.

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