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Abstract

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OXIDATION OF *n*-BUTANE IN THE GAS AND LIQUID PHASES

The considerable advantages of liquid-phase oxidation of *n*-butane ([1,2]) as compared with the gas-phase reaction require a comparative study of the mechanism of the process in the gas and liquid phases under comparable conditions. According to the viewpoint expressed by N. N. Semenov ([3]), the direction of the hydrocarbon oxidation process in the gas phase, depending on temperature and pressure, is determined by competition between radical reactions: isomerization of the radical $RO_2^\bullet$, followed by its monomolecular decomposition,

$$RO_2^\bullet \to R'HO + R''O^\bullet \qquad (1)$$

and the bimolecular reaction of $RO_2^\bullet$ with the initial hydrocarbon,

$$RO_2^\bullet + RH \to ROOH + R^\bullet. \qquad (2)$$

As the pressure in the system is increased, the density of the hydrocarbon increases and reaction (2) begins to predominate. On the basis of these ideas, one might suppose that the considerable change in the density of the substance on passing from the gaseous state to the liquid state should be the main cause of the differences in the oxidation mechanisms. However, in a recently published work ([4]) we showed that, in the oxidation of ethyl alcohol, the transition from a liquid-phase process to a gas-phase one is accompanied by such a sharp change in the composition of the reaction products that it cannot be explained within the framework of the concept of competition between radical reactions. Apparently, in this case the decisive role is played by the specific features of the liquid state of the alcohol, caused, for example, by the presence of intermolecular hydrogen bonds. For nonpolar compounds it is difficult to expect such a specific difference between the liquid and gaseous states of the substance; therefore one might think that the difference in the composition of the products of butane oxidation in the gas and liquid phases should probably be determined mainly by the value of the butane density under the given conditions.

The oxidation of butane was carried out in an autoclave-type apparatus, described in our previous papers ([2]), with an inserted glass beaker. In liquid-phase

Fig. 1. Kinetic curves for the consumption of n-butane and accumulation of oxidation products at 145°C and a pressure of 50 atm in the liquid (numbers without primes) and gas (numbers with primes) phases.

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oxidation, 100 ml of *n*-butane was charged into the reactor; on heating to the temperature of the experiment it occupied practically the entire volume of the reactor, and, consequently, the reaction in the vapors above the liquid could be neglected. In gas-phase oxidation, only a small amount of butane was charged into the reactor, creating a pressure in the system lower than the vapor pressure of its saturated vapor at the given temperature. The reaction products were analyzed by chemical methods and by paper chromatography ([5,6]).

The kinetic curves for the consumption of butane and the formation of oxidation products at 145° and a pressure of 50 atm are given in Fig. 1. The results of the analysis are presented in mole percent of the butane that reacted to form the given product, relative to the initial butane. It is evident from Fig. 1 that the induction period of the process in the gas phase is considerably ···

greater than in the liquid phase, while the reaction rate after the end of the induction period is practically the same.

The main reaction products in both cases are acetic acid, methyl ethyl ketone, and acetic acid esters. However, on going to the gas phase the relative yield of such substances as methyl alcohol and acetaldehyde increases, and appreciable amounts of carbon monoxide and formaldehyde also appear, which were completely absent in liquid-phase oxidation. Bifunctional compounds (diketone, keto alcohol), found in the products of liquid-phase oxidation of butane, disappear completely during oxidation in the gas phase.

Fig. 1. Kinetic curves for the consumption of *n*-butane and accumulation of oxidation products at 145°C and a pressure of 50 atm in the liquid (numbers without primes) and gas (numbers with primes) phases.
A –consumption of butane; **B**: 1 –acetic acid, 2 –formic acid; **V**: 1 –methyl ethyl ketone, 2 –diacetyl, 3 –acetone, 4 –acetaldehyde, 5 –formaldehyde; **G**: 1 –ethyl acetate, 2 –methyl acetate, 3 –butyl acetate, 4 –sec-butyl acetate-3-one; **D**: 1 –ethanol, 2 –methanol, 3 –butanol, 4 –2-butanol-3-one; **E**: 1 –CO_2, 2 –CO; **Zh** –peroxides.

In order to draw a conclusion as to the extent to which the composition of the products of butane oxidation under different process conditions changes in accordance with ideas about the competition of radical reactions, it is necessary to compare the rates of consumption of butane along the two reaction pathways of the radical $RO_2^{\cdot}$.

The bimolecular interaction of $RO_2^{\cdot}$ with butane can lead to the formation of hydroperoxide, methyl ethyl ketone, diacetyl, butyl alcohol, acetic acid, and its esters. The products of monomolecular decomposition of $RO_2^{\cdot}$ are aldehydes, formic acid, methyl and ethyl alcohol, CO and CO_2. Acetic acid can be formed not only by reaction (2), but also through further oxidation of acetaldehyde, which is a product of reaction (1). The same applies to carbon dioxide, which can be obtained as a result of subsequent transformations of the products of both reactions. The fraction of these substances formed by each of the two process pathways was estimated as follows. Calculating w_2 as the sum of the maximum rates of accumulation of hydroperoxide, methyl ethyl ketone, diacetyl, acetates, and butanol (without acetic acid and CO_2), and w_1 as the sum of the rates of accumulation of the decomposition products of the radical $RO_2^{\cdot}$, we obtain the ratio

$$\frac{w_2}{w_1 + w_2}$$

and assume that this ratio also determines the fraction of acetic acid and CO_2 formed by the bimolecular route.

Using the data of Table 1, which gives the values of w_1 and w_2 for all products of liquid-phase and gas-phase oxidation of butane, it is easy

to estimate the change in the direction of the process on transition from the liquid phase to the gas phase. For the liquid phase, $\frac{w_2}{w_1} = 7.8$, for the gas phase 1.02, i.e., the ratio of the rates when the aggregate state of butane changes varies by only $\sim$ 8-fold.

This is in agreement with ideas about the competition of radical reactions, since in the present case the concentration of butane changes by a factor of 6.5 (from 0.39 $\mathrm{g/cm}^3$ in the liquid phase to 0.06 $\mathrm{g/cm}^3$ in the gas phase).

Table 1

Maximum rates of accumulation of butane oxidation products formed by bimolecular (w_2) and monomolecular (w_1) reactions of the radical $RO_2\cdot$ at 145°

Reaction products	Liquid phase w_2	Liquid phase w_1	Gas phase w_2	Gas phase w_1
Acetic acid	1.73	0.22	0.94	0.93
Methyl ethyl ketone	1.32	–	0.60	–
Diacetyl	0.70	–	0.00	–
Methyl acetate	0.30	–	0.50	–

Reaction products	Liquid phase w_2	Liquid phase w_1	Gas phase w_2	Gas phase w_1
Ethyl acetate	0.85	–	0.50	–
Butyl acetate	0.45	–	0.15	–
Butanol	0.30	–	0.05	–
Keto alcohol	0.14	–	0.00	–
Hydroperoxides	0.15	–	0.15	–
Formic acid	–	0.10	–	0.20
Acetone	–	0.10	–	0.15
Acetaldehyde	–	0.05	–	0.40
Formaldehyde	–	0.03	–	0.06
Methanol	–	0.10	–	0.14
Ethanol	–	0.20	–	0.25
CO	–	0.00	–	0.70
CO_2	0.45	0.05	1.37	1.33
Total	6.39	0.82	4.26	4.16
w_2/w_1	7.8	7.8	1.02	1.02

Considering these results together with the data obtained in the oxidation of ethyl alcohol (4), one may conclude that the difference in the mechanism of liquid-phase and gas-phase oxidation of organic substances is determined not only by the external parameters of the system, but also by the specific properties of the oxidized substance itself in the liquid phase. The oxidation of butane, in this respect, is an example of a reaction in which the specificity of the liquid-phase state of the oxidized substance practically has no effect, whereas the oxidation of ethyl alcohol is an example of a reaction whose mechanism depends mainly on the specific properties of the alcohol in the liquid state.

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Note: Figure translations are in progress. See original paper for figures.

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