Doklady of the Academy of Sciences of the USSR

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1960

SovietRxiv

Abstract

Full Text

Doklady of the Academy of Sciences of the USSR
1960. Volume 133, No. 1

PHYSICAL CHEMISTRY

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ON DIFFERENCES IN THE MECHANISM OF OXIDATION OF ETHYL ALCOHOL IN THE LIQUID AND GAS PHASES

In the oxidation of *n*-butane in the liquefied state at temperatures and pressures close to the critical values, it was established that carrying out the process in the liquid phase has a number of substantial advantages over gas-phase oxidation (^{1,2}).

Liquid-phase oxidation proceeds at considerably lower temperatures, is distinguished by high selectivity, high conversion rates, and the practically complete absence of deep-oxidation products characteristic of the gas-phase process. Elucidating the causes responsible for these differences is an important scientific and practical task.

Considering the question of changes in the composition of products under different conditions of hydrocarbon oxidation in the gas phase, N. N. Semenov (^{3}) explained this change by competition between two radical reactions: isomerization of the radical $RO_2\bullet$, followed by its monomolecular decomposition,

$$RO_2\bullet \rightarrow R'O\bullet + R''OH \tag{1}$$

and the bimolecular reaction of $RO_2\bullet$ with the starting hydrocarbon

$$RO_2\bullet + RH \rightarrow RO_2H + R\bullet . \tag{2}$$

An increase in temperature and a decrease in pressure favor reaction (1), whereas a decrease in temperature and an increase in pressure favor reaction (2).

Applying these ideas to the reactions of liquid-phase oxidation, which are distinguished by high densities of the initial hydrocarbon, one must assume that the predominant direction of the reaction should be the formation of hydroperoxide (reaction 2). It is also possible that the different course of the oxidation reaction in the liquid and gas phases is a consequence not only of a change in the concentration of the substance upon changing its state of aggregation, but is also caused by more profound reasons, arising from differences in the oxidation mechanism. In this connection it is advisable to carry out a comparative study of the mechanism of gas-phase and liquid-phase oxidation using the example of one and the same reaction under comparable conditions.

One suitable object for such a study is ethyl alcohol, the liquid-phase oxidation of which, owing to its relatively high critical temperature (243°), can be studied over a wide temperature range.

The oxidation of ethyl alcohol in the liquid phase at elevated pressures is also of independent interest, since data on the kinetics of this reaction are completely absent from the literature, and there are only isolated indications (in the form of patents) of the possibility of carrying out the process in the presence of catalysts.

In the present work the oxidation of ethyl alcohol was studied in an autoclave installation made of stainless steel, with a reactor constructed in the form of

cylinder equipped with tubes for bubbling air and for taking samples of the reaction products, and with a thermocouple. The evaporating alcohol was returned to the reactor in the form of condensate from the reflux condenser (2).

For the identification and quantitative determination of the individual reaction products, both conventional methods of chemical analysis and specially developed procedures for chromatographic (on paper) separation of alcohols and carbonyl compounds (4) were used.

The oxidation reaction in the liquid phase was carried out at 200°, a pressure of 50 atm, and an air feed rate of 20 l/hr. The transition to oxidation in the gas phase at the same temperature was effected by lowering the pressure in the reactor to 20 atm.

The kinetic curves for the consumption of ethyl alcohol and the accumulation of its oxidation products in the gas and liquid phases are shown in Fig. 1. For convenience of comparison, all the results presented in Fig. 1 are referred to one unit amount of the initial alcohol. Liquid-phase oxidation is characterized by the practically complete absence of an induction period; in gas-phase oxidation a long induction period is observed (on the order of 10 hr), after which the process proceeds at a considerably lower rate than in oxidation in the liquid phase.

A detailed analysis of the reaction products indicates a sharp difference in the composition of the substances formed during the oxidation of ethyl alcohol in the gas and liquid phases. Acetic acid and ethyl acetate, which are the main reaction products in the liquid phase, are practically absent during oxidation in the gas phase. Carbon monoxide is formed in very large amounts only in gas-phase oxidation. The second principal product of gas-phase oxidation of

Figure 1

Figure 1: Figure 1

alcohol is acetaldehyde, which, during oxidation in the liquid phase, is detected only in small amounts as an intermediate reaction product.

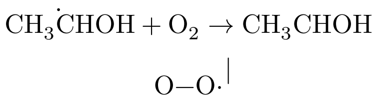
Formic acid and peroxide compounds are detected in very small amounts in both cases, which apparently is connected with their low stability under the conditions of our experiments. Formic acid decomposes thermally (to CO and water), and the peroxide

Fig. 1. Kinetic curves for the accumulation of reaction products during oxidation of ethyl alcohol at 200° in the liquid phase (numbering without primes) and in the gas phase at an initial concentration of ethyl alcohol $2.6 \cdot 10^{-3}$ mol/cm^3 (numbering with primes). 1 and $1'$—consumption of ethyl alcohol (the light points on curve $1'$ correspond to the kinetic curve for alcohol consumption in experiments with an initial concentration of $0.54 \cdot 10^{-3}$ mol/cm^3, conditionally shifted to the same induction-period value as in the experiments with concentration $2.6 \cdot 10^{-3}$ mol/cm^3); $2, 2'$—acetic acid; $3, 3'$—formic acid (right-hand scale); $4, 4'$—ethyl acetate; $5, 5'$—ethyl formate (right-hand scale); $6, 6'$—acetaldehyde; $7, 7'$—formaldehyde (right-hand scale); $8, 8'$—CO_2; $9, 9'$—CO; $10, 10'$—peroxide; $11, 11'$—methyl alcohol.

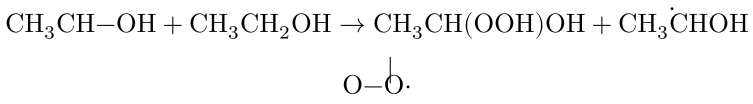
compounds—under the catalytic influence of the metallic wall of the reactor. Formaldehyde and methyl alcohol are products characteristic only of gas-phase oxidation.

Such a sharp change in the direction of the reaction on going from liquid-phase oxidation to gas-phase oxidation appears, at first glance, to be in accord with Semenov' s ideas on the competition of radical reactions. The main reactions occurring in the liquid-phase oxidation of ethyl alcohol may be represented as follows:

$$CH_3CH_2OH + O_2 \rightarrow CH_3\dot{C}HOH + HO_2$$



$$CH_3\dot{C}HOH + O_2 \rightarrow CH_3\underset{\substack{| \\ O-O\cdot}}{C}HOH$$

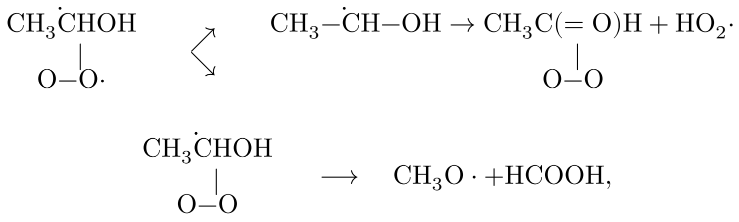


$$CH_3\underset{\substack{| \\ O-O\cdot}}{C}H-OH + CH_3CH_2OH \rightarrow CH_3CH(OOH)OH + CH_3\dot{C}HOH$$

$$CH_3CH(OOH)OH \rightarrow CH_3COH + H_2O_2; \quad CH_3COH \xrightarrow{O_2} CH_3COOH.$$

In this case the main reaction product should be acetic acid, which is also confirmed by the experimental results obtained in the present work. (Ethyl acetate should be regarded as a product of the further interaction of acetic acid with ethyl alcohol.)

On going over to gas-phase oxidation at the same temperature, the density of the reacting mixture decreases and monomolecular decomposition of the peroxide radical becomes more probable. Apparently, two paths of isomerization of the radical are possible,



$$\underset{\mathrm{O{-}O\cdot}}{\underset{|}{\mathrm{CH_3\dot{C}HOH}}} \quad \begin{matrix}\nearrow \\ \searrow\end{matrix} \quad \mathrm{CH_3{-}\dot{C}H{-}OH} \rightarrow \mathrm{CH_3}\underset{\mathrm{O{-}O}}{\underset{|}{\mathrm{C}}}\mathrm{(=O)H} + \mathrm{HO_2\cdot}$$

$$\underset{\mathrm{O{-}O}}{\underset{|}{\mathrm{CH_3\dot{C}HOH}}} \longrightarrow \mathrm{CH_3O\cdot + HCOOH},$$

leading to the products of the gas-phase oxidation of ethyl alcohol observed experimentally: acetaldehyde and formic acid (carbon oxides).

Under these conditions acetaldehyde is the final reaction product and is not oxidized to acetic acid, probably because of the inhibiting action of ethyl alcohol, which is characteristic of gas-phase oxidation. However, a change in the density of ethyl alcohol cannot serve as the sole explanation of the observed difference between the oxidation mechanism in the gas and liquid phases. Under the conditions of our experiments, the concentration of alcohol on transition from one aggregate state to the other changes only by a factor of 5 (from $1.26 \cdot 10^{-2}$ mol/cm^3 in the liquid phase to $2.6 \cdot 10^{-3}$ mol/cm^3 in the gas phase), which should not have led to so strong a change in the direction of the reaction. Indeed, the ratio of the rates of reactions (1) and (2) at one and the same temperature should change in proportion to the change in the concentration of the alcohol being oxidized,

$$\frac{w_1}{w_2} = \frac{k_1(R)}{k_2(R)(ROH)},$$

i.e., in our case the ratio w_2/w_1 in oxidation in the gas phase should have been 5 times smaller than in the liquid phase. To estimate the value of k_2/k_1 from the experimental data, let us introduce the concept of the specific fraction of products formed along each of the two reaction directions: by decomposition of the peroxide radical

$$\alpha_1 = \frac{w_1}{w_{\text{obr}}}$$

and by its interaction with alcohol

$$\alpha_2 = \frac{w_2}{w_{\text{obr}}},$$

where $w_{\text{obr}} = w_1 + w_2$ is the total rate, composed of

rates of formation of products characteristic of gas-phase and liquid-phase oxidation. The relation between α_1 and α_2 and the ratio of the constants k_2/k_1 is found from the condition of a stationary concentration of radicals R

$$\frac{d(\text{R}\cdot)}{dt} = w_{\text{form}} - k_1(\text{R}) - k_2(\text{R})(\text{ROH}) = 0. \tag{I}$$

Substituting into the expressions for w_1 and w_2 the value of (R) from equation (I), we obtain

$$w_1 = \frac{w_{\text{form}}}{1 + \frac{k_2}{k_1}(\text{ROH})} \quad \text{and} \quad w_2 = \frac{w_{\text{form}}(\text{ROH})}{\frac{k_1}{k_2} + (\text{ROH})}$$

or

$$\alpha_1 = 1\Big/\left[1 + \frac{k_2}{k_1}(\text{ROH})\right]; \quad \alpha_2 = (\text{ROH})\Big/\left[\frac{k_1}{k_2} + (\text{ROH})\right].$$

Knowing the values of α, from the experimental data we determine the values of k_2/k_1 for the liquid-phase and gas-phase oxidation of alcohol. In the first case $k_2/k_1 = 0.37$, and in the second $4.8 \cdot 10^{-4}$, i.e., the ratio of the rates of reactions (1) and (2) upon transition from the liquid phase to the gas phase changes not by a factor of 5, but by approximately 10^3 times.

A fivefold change in the alcohol concentration (from $2.6 \cdot 10^{-3}$ mol/cm^3 to $0.54 \cdot 10^{-3}$ mol/cm^3) during oxidation in the gas phase (200° and a pressure of 20 atm.) leads to an increase in the induction period from 10 to 24 hours and has practically no effect either on the rate of alcohol consumption after the end of the induction period (open circles in Fig. 1), or on the composition of the oxidation products. At the same time the values of α_1 and α_2 change only by a few times.

Thus it may be concluded that the principal factor determining the rate and direction of the liquid-phase oxidation of ethyl alcohol is not only the relatively high density characteristic of the liquid phase, but also the specificity of the liquid state of the substance. This specificity may be due, for example, to the influence of intermolecular hydrogen bonds or to the presence of reactions involving ions, which are absent in the gas phase.

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Received
29 III 1960

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