PHYSICAL CHEMISTRY

E. A. Bliumberg, M. G. Bul' ygin, L. Ya. Margolis,

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

E. A. Bliumberg, M. G. Bul' ygin, L. Ya. Margolis,
Corresponding Member of the Academy of Sciences of the USSR N. M. Emanuel'

LIQUID-PHASE OXIDATION OF ISOBUTYLENE IN THE PRESENCE OF HETEROGENEOUS CATALYSTS

The principle of carrying out oxidation processes of hydrocarbon gases in the liquefied state (^{1}) is a highly effective method for the direct synthesis of many valuable chemical products. Thus, in the liquid-phase oxidation of *n*-butane, the main product of the reaction is acetic acid. Methyl ethyl ketone and ethyl acetate are also formed in considerable amounts (^{2}). The yield of these substances reaches 60–70% of the reacted butane. However, the complete composition of the reaction products remains rather complex because of the large number of by-products formed during butane oxidation (acetone, formic acid, alcohols C_1—C_4, esters of acetic acid, etc.).

In this connection, it is of interest to determine the possibility of increasing the selectivity of liquid-phase oxidation processes of hydrocarbon gases by using heterogeneous catalysts.

In undertaking such a study, we proceeded from the premise that liquid-phase oxidation of hydrocarbons has no fundamental differences from analogous reactions in the gas phase. We are led to this conclusion by the results of work (^{2}), in which the oxidation process of *n*-butane was studied in the gas and liquid phases under comparable conditions (temperature 145°, pressure 50 atm). It was shown that, in passing from liquid-phase oxidation to gas-phase oxidation, the composition of the reaction products (the direction of the process) changes in accordance with ideas concerning the influence of hydrocarbon concentration on the competition between two reactions of the peroxide radical RO_2, which carries out the chain process (^{3})

$$\mathrm{RO_2 + RH \rightarrow RO_2H + R\cdot;\quad RO_2 \rightarrow R'CHO + R''O:}$$

In other words, the difference in the composition of the products of liquid-phase and gas-phase oxidation of butane under identical process conditions is determined only by the different concentration of butane in the gas and liquid phases. Consequently, it could be expected that heterogeneous catalysts active in gas-phase hydrocarbon oxidation reactions would also prove effective for liquid-phase oxidation reactions.

Liquid-phase heterogeneous oxidation of hydrocarbons has been studied very little. It was shown in (^{4}) that additions of metallic (Ag, Ni, Cu, etc.) and oxide (CuO, MnO_2, V_2O_5, etc.) catalysts shorten the induction period of the liquid-phase oxidation of aromatic and *n*-paraffinic hydrocarbons. In the oxidation of olefins (cyclohexene and methyl-2-butene-2) in the liquid phase in the presence of oxides of copper, manganese, chromium, and others, the principal reaction products are the corresponding hydroperoxides (^{5}).

In the present work, isobutylene was chosen as the object of study, since heterogeneous oxidation of olefins has been studied rather fully (^{6}). As catalysts, metal oxides and complex salts listed in Table 1 were investigated.

All these catalyst samples are characterized by high catalytic activity in the processes of gas-phase oxidation of various hydrocarbons.

Table 1 also gives the specific surface areas and amounts of the catalysts used in our experiments. For the oxidation, 99.8% isobutylene was used with an admixture of 0.1 wt.% butylene and 0.1% saturated hydrocarbons C_3—C_4. The experiments were carried out in an autoclave-type apparatus made of stainless steel, with a magnetic turbine stirrer (stirrer speed up to 1420 rpm, power 0.6 kW).

Table 1

Catalyst	Amount, wt.%	Specific surface area, m^2/g
Electrolytic MnO_2	0.1—2.0	56
Cr_2O_3	0.4	40
$CuCr_2O_4$	1.0	5.0
$MnCr_2O_4$	1.2	3.0
V_2O_5	0.1—1.0	1.5
CuO	0.3	1.2
$MnCoO_4$	0.4	0.7
Pt on SiO_2	0.1—1.0	200

Into the reactor of the apparatus were charged 150 ml of liquefied isobutylene and a weighed portion of solid catalyst; the apparatus was sealed, heating of the reactor was switched on, and, at 140° and a pressure of 50 atm, air was bubbled through at a rate of 20 l/h for a prolonged period. During the process, samples of the reaction liquid were taken and analyzed both by chemical methods (titration of acids with alkali, reaction with hydrochloric-acid hydroxylamine for carbonyl compounds, etc.) and by gas-liquid (^{7}) chromatography and paper chromatography (^{8}, ^{9}).

In the absence of catalysts, the liquid-phase oxidation of isobutylene under these conditions does not begin even 12 hours after the introduction of air.

Fig. 1. Kinetic curves for the accumulation of products during liquid-phase oxidation of isobutylene at a temperature of 140° and a pressure of 50 atm in the presence of 0.1 wt.% MnO_2 (numbers without primes) and upon initiation with dinitrile of azoisobutyric acid (numbers with primes): 1, 1′—acids; 2, 2′—carbonyl compounds.

Fig. 2. Chromatograms of a mixture of products of liquid-phase oxidation of isobutylene at a temperature of 140°, pressure 50 atm: 1—in the presence of 0.1 wt.% MnO_2; 2—upon initiation with dinitrile of azoisobutyric acid.

When any of the catalysts listed in Table 1 is introduced, the oxidation of isobutylene proceeds practically entirely without an induction period, with considerable amounts of oxygen-containing compounds being formed; the principal products of this reaction are acetone and formic acid. In small amounts, compounds are also formed that retain in their···

in the molecule an unsaturated bond (acrylic and methacrylic acids, allyl and methallyl alcohols, etc.).

To clarify the question of the selectivity of the action of heterogeneous catalysts, in parallel with these experiments we carried out experiments in which an initiator—azobisisobutyronitrile—was used to eliminate the induction period of the liquid-phase oxidation of isobutylene. Figure 1 gives kinetic curves for the accumulation of products in the initiated oxidation of isobutylene (Fig. 1, curves 1, 2) and in oxidation in the presence of 0.1 wt. % $\mathrm{MnO_2}$ (curves 1′ and 2′). As is evident from the figure, practically no difference is observed in the kinetics of these two reactions. The chromatograms of the reaction-product mixture, corresponding to the same degree of conversion of isobutylene in initiated and catalyzed oxidation (Fig. 2), lead us to the same conclusion. In both cases, the peaks of the individual components of the reacting mixture of oxidation products are identical in retention time and in height.

All the catalysts investigated gave the same result. Thus, under the conditions of our experiments, the heterogeneous catalysts prove to be only initiators of the isobutylene oxidation process and possess no selectivizing action.

This result is in agreement with data obtained in work (5), whose authors, on the basis of a comparison of the rates of oxidation of olefins in the presence of initiators (benzoyl peroxide, azobisisobutyronitrile) and heterogeneous catalysts (CuO, $\mathrm{MnO_2}$), come to the conclusion that in the liquid phase the catalysts act only as initiators, without changing the mechanism of the process.

Thus, a simple transfer of ideas about heterogeneous catalysis of gas-phase oxidation reactions to reactions in the liquid phase proves to be impossible.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
20 III 1963

REFERENCES

1. N. M. Emanuel, *DAN*, **110**, 245 (1956).
2. E. A. Blyumberg, G. E. Zaikov, N. M. Emanuel, *Neftekhimiya*, **1**, No. 2, 235 (1961).
3. N. N. Semenov, *On Certain Problems of Chemical Kinetics and Reaction Capacity*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 85.
4. I. Burger, M. C. Meyer et al., *C. R.*, **252**, 2235 (1961).
5. C. Kröger, A. Keller, *Oil u. Kohle*, **40**, 609 (1945); **43**, 241 (1948); **55**, 955 (1960).
6. L. Ya. Margolis, *Heterogeneous Catalytic Oxidation of Hydrocarbons*, Moscow, 1962.
7. E. A. Blyumberg, Yu. D. Norikov, E. S. Smirnov, *Neftekhimiya*, **2**, No. 6 (1962).
8. G. E. Zaikov, *Zhurn. anal. khim.*, **15**, 104, 639 (1960).
9. P. K. Obukhova, in: *Oxidation of Hydrocarbons in the Liquid Phase*, Publishing House of the Academy of Sciences of the USSR, 1959, p. 249.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.