Soviet-era science, translated into English

Reports of the Academy of Sciences of the USSR

CHEMISTRY

1963

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196301.87176

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

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1963. Volume 152, No. 3

CHEMISTRY

L. P. Shapovalova, Ya. B. Gorokhovatskii, M. Ya. Rubanik

Effect of Products on the Rate of Oxidation of Isobutylene on a Copper Catalyst

(Presented by Academician A. A. Balandin, 31 V 1963)

A number of works ($^{1-3}$) have shown that, in the heterogeneous catalytic oxidation of organic substances, the reaction products can exert an inhibiting influence on the course of the process. In particular, it was established that the oxidation of propylene on a copper catalyst is considerably slowed by the acrolein and water that are formed (^{3}). Some works point to the selectivizing action of water vapor on the oxidation of propylene (^{4,5}). In patents, for example (^{6}), the use of water vapor as a diluent in the oxidation of olefins is recommended.

The purpose of the present work was to study the influence of products on the rate of oxidation of isobutylene on a copper catalyst.

The investigation was carried out by the flow-circulation method in an apparatus and according to a procedure described in (^{2,3,7}). As cooling agents for freezing water vapor out of the cycle, ice, melting ethylene glycol (m.p. $< -12°$), carbon tetrachloride (m.p. $< -23°$), and dichloroethane (m.p. $-35°$) were used. When water vapor and methacrolein were removed together, the freezing traps were immersed in melting *n*-octane (m.p. $-55°$). Experiments on the influence of additions of water vapor were carried out in the apparatus described in (^{5}). The catalyst—copper oxide deposited on impure carborundum (Globar)—contained, per liter of volume, 2.9 g of Cu (0.22% of the weight of the support); its bulk weight was 1.33 g/ml. The investigation was carried out on isobutylene-oxygen-nitrogen mixtures.

The rate of the process (W) was determined as the number of moles of substance formed per unit time (sec) per unit volume of catalyst (ml). The selectivity (S) was calculated as the ratio of the amount of isobutylene converted into methacrolein to the total amount of isobutylene that had reacted.

All experiments were conducted under conditions excluding the influence of macrokinetic factors, which was checked by special experiments. To determine which of the isobutylene oxidation products (methacrolein, water, carbon dioxide) inhibits the process, the method was used

Table 1

Influence of reaction products on the rate of oxidation of isobutylene *(Catalyst volume 4 ml; isobutylene concentration 6.95 vol.%; flow rate 290–300* cm^3/min*)*

No.	Amount of O_2 at inlet, vol.%	Cycle concentration, vol.%: O_2	Cycle concentration, vol.%: carbonyl comp.	Cycle concentration, vol.%: CO_2	Products removed	S, %	$W_1 \cdot 10^6$, mol/ml· sec	$W_2 \cdot 10^6$, mol/ml· sec
$t =$ 350°								
1	7,65	3,05	0,29	0,60	–	66	0,156	0,322
2	–	3,25	0,18	1,35	H_2O, C_4H_6O	63	0,318	0,742
$t =$ 365°								
3	6,40	4,15	0,44	1,00	–	65	0,251	0,547
4	8,80	3,70	0,16	2,30	H_2O, C_4H_6O	63	0,541	0,256
5	8,80	3,70	–	0,10	H_2O, C_4H_6O, CO_2	–	–	–
$t =$ 380°								
6	–	3,95	0,62	1,75	–	59	0,309	0,875
7	–	4,25	0,56	1,50	–	59	0,275	0,735
8	–	4,00	0,21	3,35	H_2O, C_4H_6O	63	0,787	1,830

selective removal of products from the cycle (2) while maintaining a constant concentration of the initial substances in the cycle or in the gas mixture being fed. From the data of Table 1 it is evident that, when water and methacrolein are removed (Nos. 1–4, 6–8), the rate of formation of methacrolein (W_1) and carbon dioxide (W_2) increases significantly. When, in addition, carbon dioxide is also removed (No. 5), and when a gas mixture of the same composition is kept at the inlet to the cycle, the oxygen concentration in the cycle remains the same as when methacrolein and water are removed. Consequently, CO_2 has no appreciable effect on the reaction rate.

The results of experiments on the effect of water vapor on the rate of the process are presented in Figs. 1 and 2. From Fig. 1 it is evident that removal of water vapor from the reaction zone leads to a sharp increase in the rate of formation

SovietRxiv

Fig. 3

Figure 1: Fig. 3

of carbon dioxide. From the course of the curves in Fig. 2 it is evident that water also has a weak inhibiting effect on the formation of methacrolein. With increasing temperature this effect decreases, and already at 380° removal of water vapor does not lead to a change in the rate of formation of methacrolein.

Fig. 1. Dependence of the rate of formation of carbon dioxide on the pressure of water vapor in the reaction zone: 1, 2, 3 —upon removal from the cycle of water; 4, 5 —upon removal from the cycle of water and methacrolein. Concentrations in the cycle: isobutylene —20 vol.%, oxygen —6.0 vol.%. *A* —at 340°, *B* —365°, *C* —380°.

For comparison of the action of water vapor and methacrolein vapor on the rate of oxidation of isobutylene, we plotted on the graphs of Figs. 1 and 2 the data obtained by us when methacrolein and water were removed together from the reaction zone. It turned out that the rate of formation of carbon dioxide when methacrolein and water are removed increases to almost the same extent as when only water vapor is removed (Fig. 1). Hence it may be concluded that the deep oxidation of isobutylene is inhibited only by water vapor. Comparison of analogous data in Fig. 2 shows that removal of methacrolein and water leads to a much sharper increase in the rate of formation of methacrolein than removal of only water vapor. Consequently, the partial oxidation of isobutylene is inhibited mainly by the methacrolein formed.

Fig. 2. Dependence of the rate of formation of methacrolein on the pressure of water vapor in the reaction zone. Concentrations in the cycle: isobutylene — 20 vol.%, oxygen —6.0 vol.%. Designations are the same.

In connection with the data obtained, it was of interest to examine the effect of additions of water vapor on the oxidation of isobutylene. From the data of Table 2, in which

the results of these experiments are presented, it is seen that introducing 30% water vapor into the initial mixture leads, at 330–420°, to suppression of the deep oxidation reaction of isobutylene. The rate of incomplete oxidation of isobutylene at temperatures below 365° changes hardly at all, and at 420° even increases somewhat upon the introduction of water vapor into the mixture. In accordance with this, introducing water vapor into the initial mixture (in our case from 0.10 to 30 vol.%, or from 0.8 to 260 mm Hg) invariably increases the selectivity of the process (Fig. 3 and Table 2).

Fig. 3. Dependence of the selectivity of isobutylene oxidation on the pressure of water vapor in the reaction zone. Concentrations in the cycle: isobutylene — 20 vol.%, oxygen —6.0 vol.%. Designations are the same.

From the results we obtained on the different action of water on the reaction

Fig. 4

Figure 2: Fig. 4

of deep and mild oxidation of isobutylene, its selectivizing effect on the process becomes clear.

As was indicated (^{3}), the flow-circulation method makes it possible to find the values of the heats of activation* of the reaction without knowing the kinetic equation of the process. For this it is necessary to keep the concentrations of the initial substances in the cycle or at the inlet constant and, if the products inhibit the process, to remove them from the reaction zone. Then an equation of the form $W = k \cdot e^{-E/RT} f(C)$ is transformed into the equation

$$W = k' \cdot e^{-E/RT},$$

since the quantity $k' = k \cdot f(C)$ is constant. From the slope of the straight lines $\lg W - 1/T$, the value of the heat of activation can be calculated. Using this method, we determined (Fig. 4) the heats of activation of formation of methacrolein and carbon dioxide, respectively: $E_1 = 14$-16 kcal/mole, $E_2 = 19$-21 kcal/mole. The heats of activation of propylene oxidation, determined under analogous conditions (^{3}), are, respectively, $E_1 = 20$ kcal/mole, $E_2 = 26$ kcal/mole. The smaller value of the heats of activation for the formation of the oxidation products of isobutylene as compared with propylene may be connected with stronger adsorption of isobutylene on the copper catalyst than that of propylene. Owing to this, the C—C and C—H bonds in the isobutylene molecule become less strong than in the propylene molecule, which facilitates, in comparison with the latter, the formation of aldehyde and carbon dioxide.

Fig. 4. Dependence of $\lg W_1$ (1) and $\lg W_2$ (2) on $1/T$ upon removal from the reaction zone of products that inhibit the process

On the basis of the results of the investigation we carried out, some conclusions may be drawn about the scheme by which the process proceeds. In our opinion, the oxidation of isobutylene (as also of propylene (^{3})) proceeds according to a parallel-consecutive scheme, i.e., at low temperatures there is parallel oxidation of isobutylene to methacrolein and carbon dioxide, while with increasing temperature this process is accompanied by further oxidation of the methacrolein formed. Indeed, the addition of 30% water vapor to the initial mixture at 330-365° leads practically to no change in the rate of formation of methacrolein, which would necessarily be observed if there occurred oxidation of the latter. With increasing temperature, the methacrolein formed begins to undergo further oxidation. As is seen from Fig. 2, already at 380°,

* By the term "heat of activation" the authors mean the observed apparent activation energy (Ukr. Khim. Zhurn., **21**, 296, 1955).

when water is removed from the reaction zone the observed rate of methacrolein formation does not change, although in fact it should have increased, since water nevertheless inhibits the formation of methacrolein, as we observed at low temperatures. Apparently, methacrolein is partially further oxidized; therefore we do not observe an increase in the rate of its formation when water is removed.

Table 2

Effect of additions of water vapor on the rate of oxidation of isobutylene

(Catalyst volume 4 ml; isobutylene concentration 18–20 vol. %, oxygen 4.7–5.0 vol. %; flow rate 265–280 cm^3/min)

No.	H_2O	C_4H_6O	CO_2	S, %	$W_1 \cdot 10^6$, mol/ml·sec	$W_2 \cdot 10^6$, mol/ml·sec	Determination No.
t = 330°	*t = 330°*	*t = 330°*	*t = 330°*	*t = 330°*	*t = 330°*	*t = 330°*	*t = 330°*
1	0.85	0.35	0.50	73	0.174	0.251	15
2	0.81	0.31	0.50	71	0.156	0.251	17
3	30.70	0.32	0.14	90	0.163	0.072	14
4	30.70	0.35	0.14	90	0.180	0.072	16
5	30.70	0.32	0.10	92	0.165	0.052	18
t = 365°	*t = 365°*	*t = 365°*	*t = 365°*	*t = 365°*	*t = 365°*	*t = 365°*	*t = 365°*
6	1.29	0.39	0.90	64	0.215	0.472	2
7	1.74	0.54	1.20	65	0.288	0.625	5
8	1.80	0.55	1.25	66	0.288	0.655	12
9	30.70	0.60	0.35	88	0.323	0.180	1
10	30.70	0.64	0.40	87	0.314	0.193	3
11	30.70	0.58	0.40	85	0.275	0.193	4
12	30.85	0.58	0.40	85	0.280	0.193	11
13	31.40	0.70	0.40	88	0.350	0.201	13
t = 420°	*t = 420°*	*t = 420°*	*t = 420°*	*t = 420°*	*t = 420°*	*t = 420°*	*t = 420°*
14	5.16	1.01	4.15	49	0.543	2.150	6
15	5.13	1.03	4.10	50	0.545	2.150	9
16	34.80	1.35	2.30	70	0.755	1.280	7
17	34.60	1.33	1.95	74	0.760	1.080	8
18	34.00	1.33	2.05	72	0.715	1.100	10

At still higher temperatures, the addition of water vapor even causes an increase in the rate of incomplete oxidation of isobutylene (Table 2, Nos. 14–18). The mechanism of this phenomenon is not yet clear. However, one of the causes is probably the suppression of the consecutive stage of further oxidation of methacrolein, as a result of which the observed rate of its formation increases when water vapor is introduced into the initial mixture.

The elucidation of the principal kinetic regularities of the oxidation of isobutylene will be the subject of the next communication.

Institute of Physical Chemistry
named after L. V. Pisarzhevskii
Academy of Sciences of the Ukrainian SSR

Received
30 V 1963

CITED LITERATURE

1. S. Ya. Pshezhetskii, S. A. Kamenetskaya, ZhFKh, **23**, 136 (1949); T. Ikawa, M. Matsumoto, N. Nagasako, *Kagaku Kogaku*, *Chem. Engng.* (Japan) **23**, 291 (1959); RZhKhim, 1960, 34103; V. Ya. Vol' fson, G. P. Korneichuk, V. A. Roiter, *Ukr. Khim. Zhurn.*, **26**, No. 3, 305 (1960); V. A. Roiter, V. P. Ushakova et al., *Kinetics and Catalysis*, **2**, 94 (1961).

2. Ya. B. Gorokhovatskii, M. Ya. Rubanik, K. M. Kholyavenko, DAN, **125**, 83 (1959).

3. V. M. Belousov, Ya. B. Gorokhovatskii, M. Ya. Rubanik, *Kinetics and Catalysis*, **3**, 221 (1962).

4. A. G. Polkovnikova, B. D. Kruzhalov et al., *Kinetics and Catalysis*, **3**, issue 2, 252 (1962).

5. E. N. Popova, Ya. B. Gorokhovatskii, DAN, **145**, No. 3, 570 (1962).

6. British Patent 640383, 19/VII, 1950; Danish Patent 69025, 15/XII, 1951; FRG Patent 875522, 4/V, 1953; British Patent 864666, 6/IV, 1961.

7. B. G. Eremina, *Gas Analysis*, L., 1955, p. 61.

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

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