# PHYSICAL CHEMISTRY

O. A. GOLOVINA, O. V. ISAEV, and M. M. SAKHAROV

1962

SovietRxiv

## Abstract

## Full Text

# PHYSICAL CHEMISTRY

**O. A. GOLOVINA, O. V. ISAEV, and M. M. SAKHAROV**

## INVESTIGATION OF THE MECHANISM OF THE OXIDATION OF PROPYLENE TO ACROLEIN ON A CUPROUS-COPPER CATALYST BY THE METHOD OF RADIOACTIVE TRACERS

*(Presented by Academician V. N. Kondrat' ev, 15.VIII.1961)*

Until recently there had been no published works on the mechanism of the catalytic oxidation of propylene to acrolein. Only very recently have several reports appeared ($^{1-3}$) devoted to this question. On the basis of kinetic and radiometric data, O. V. Isaev, L. Ya. Margolis, S. Z. Roginskii, and I. S. Sazonova came to the conclusion that the oxidation of propylene to acrolein proceeds by a parallel–consecutive scheme, with predominant formation of $CO_2$ from acrolein. V. S. Belousov, Ya. B. Gorokhovatskii, M. Ya. Rubanik, and A. V. Gershingorn, on the basis of the results of a kinetic study, believe that at high temperatures (380°) propylene is oxidized by a parallel–consecutive scheme, whereas at a lower temperature (320°) oxidation proceeds by a parallel scheme. More reliable data on the mechanism of the process can be

**Table 1**

| No. of experiment | Temp. °C | Content of $CO_2$ in exit gas, % | $v$, $p_{CO_2}$, ml/min · mg $BaCO_3$ ($a_1$) | Acrolein, % in feed gas | Acrolein, % in exit gas | Acrolein, % not activated in exit gas | $v$, $p_{\text{acrolein}}$, ml/min · mg $BaCO_3$ ($a_2$) | Film: amount of carbon, mg | Film: $v$, ml/min · mg $BaCO_3$ ($a_3$) | Amount of undecomposed labeled acrolein, % | $a_2/a_1$ | Fraction of parallel pathway, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 374 | 3.2 | 18 | 0.18 | 0.70 | 0.59 | 52 | – | 0 | 67.0 | 2.89 | 66 |
| 2 | 345 | 2.0 | 28 | 0.18 | 0.56 | 0.44 | 66 | 4.1 | 0 | 66.3 | 2.36 | 57 |
| 3 | 342 | 0.9 | 56 | 0.16 | 0.60 | 0.49 | 59 | 1.5 | 0 | 68.3 | 1.05 | 5 |
| 4 | 342 | 0.9 | 100 | 0.35 | 0.73 | 0.48 | 107 | 5.0 | 0 | 71.0 | 1.07 | 6.5 |
| 5 | 347 | 1.1 | 119 | 0.44 | 0.95 | 0.64 | 104 | – | 0 | 71.0 | 0.88 | – |
| 6 | 342 | 0.9 | 113 | 0.50 | 0.95 | 0.58 | 125 | 3.2 | 2 | 75.6 | 1.10 | 9 |
| 7 | 341 | 1.0 | – | – | 0.55 | 0.55 | – | 2.8 | – | – | – | – |

obtained by applying the method of labeled atoms. However, the results of the work ($^2$), in which this method was used, were obtained under conditions far removed from the optimum conditions of synthesis. In the initial synthesis gas, 3.5–5% acrolein was introduced, whereas normally, in the oxidation of propylene over a cuprous-copper catalyst, the gas at the reactor outlet contains only about 1% acrolein.

In the present investigation, which is a continuation of work ($^2$), the study of the mechanism of acrolein synthesis by the method of radioactive tracers was carried out under the conditions customary for this process on a cuprous-copper catalyst. Propylene and acrolein labeled with radiocarbon $C^{14}$ were used as labeled compounds. The process was studied in a flow apparatus at atmospheric pressure and a temperature of 340–347° on a catalyst containing 1% Cu on silica gel with a small addition of Ag. The reactor was charged with 3 ml of catalyst. The contact time in all experiments was 0.5 sec. The initial gas mixture of composition $C_3H_6 : O_2 : N_2 = 40 : 10 : 50$ was fed into the reactor at a linear velocity of ~7 cm/sec. It had previously been shown that under these conditions the oxidation of propylene proceeds in the kinetic region ($^4$).

Chemical analysis and analysis of the radioactivity of the products were carried out as described previously ($^2$). At the end of each experiment, gas was pumped out of the reactor at 400°C to a pressure of $10^{-2}$ mm Hg, after which the organic film was burned off from the catalyst surface with oxygen at the same temperature. The carbon dioxide obtained was converted into $BaCO_3$, from the weight and radioactivity of which the amount and specific radioactivity of the organic film were determined. The activity of the catalyst was periodically checked on a standard mixture of starting gases without radioactive additions (experiments Nos. 7 and 9, Tables 1 and 2).

## Experimental part

**Experiments with labeled acrolein** were carried out at a constant contact time, constant temperature, and the same ratio of gases in the starting mixture. Only the concentration of the added labeled acrolein in the initial gas was varied, within the range 0.16–0.5 vol. %. The labeled acrolein, synthesized by us from glycerol ($^5$), was fed into the reactor from a trap through which the initial gas mixture was passed. The required vapor pressure of the acrolein being introduced was achieved by immersing the trap with acrolein in a cooling mixture of the corresponding temperature.

All experiments were begun after the catalyst had been heated in a stream of the working gas mixture for 1 hour. In experiment No. 1, the starting gas mixture without acrolein was fed; in experiment No. 2, for the first 30 min without acrolein and for the next 30 min with acrolein; and in experiments Nos. 3–6, during the entire preliminary heating of the catalyst the starting gas mixture was fed into the reactor with an addition of acrolein of the same concentration as was then maintained in the experiment. In preliminary experiments, within the accuracy of the radioactivity measurements, no radioactivity was detected in the propylene at the reactor outlet. In the reaction products, practically only $CO_2$ and acrolein were found. The results obtained in the experiments with labeled acrolein are given in Table 1; from these data it is seen that in the first two experiments with the addition of labeled acrolein there was considerably greater formation of $CO_2$ than in all the other experiments, where the $CO_2$ concentration in the gas at the reactor outlet was practically the same ($\sim 1\%$). The concentration of $CO_2$ in these first experiments was, respectively, 3 and 2 times greater than in the subsequent ones. The amount of acrolein formed, as follows from the difference between the concentrations of acrolein in the off-gas and in the gas fed to the reactor (allowing for acrolein decomposed to $CO_2$), in all the experiments carried out did not go beyond 0.44-0.59 vol. %. The significant amounts of $CO_2$ and the reduced selectivity of the process in experiments Nos. 1 and 2, in view of the stable operation of the catalyst with constant and considerably greater selectivity in experiments Nos. 3-7, apparently indicate that in the first experiments the catalyst had not yet reached a stationary state. It is also not excluded that this is connected with the differences, noted above, in the preliminary treatment of the catalyst in these experiments and in experiments Nos. 3-6.

It is essential that only in experiments Nos. 1 and 2 is significant formation of $CO_2$ observed by a parallel route, in addition to its formation from acrolein. This is indicated by the value of the ratio of the specific radioactivities (s.r.) of acrolein and $CO_2$. In experiments Nos. 1 and 2 it is equal to 2.9 and 2.3, respectively, while in all the other experiments it is close to unity. From the radiometric data it follows that in experiment No. 1, 66%, and in No. 2, 57% of all the $CO_2$ was formed from propylene, bypassing the stage of acrolein formation. As follows from the practically identical s.r. of acrolein and $CO_2$, in experiments Nos. 3-6 the parallel pathway of $CO_2$ formation, if it exists, accounts for no more than 5-10% of the total conversion of propylene.

The organic film formed on the catalyst surface during the oxidation of propylene, in all experiments with the addition of labeled ac-

acrolein showed no radioactivity. Only in the experiment with the addition of 0.5 vol.% labeled acrolein (at the reactor outlet, 0.95 vol.% acrolein) did the radiometric data indicate that about 1% of the film was formed from acrolein. From work (2) it is known that, at an acrolein concentration of 3.5–5.0%, its share in film formation becomes significant. Thus, under conditions approaching those of the technical process, acrolein from the gas phase practically does not participate in film formation. It also follows from the data obtained that a threefold increase in the concentration of labeled acrolein in the feed gas has no noticeable effect on the amount of film formed and practically does not affect the yield of acrolein. The latter indicates the absence of a decrease in the rate of acrolein formation by the acrolein added to the feed gas. The absence of noticeable changes in the concentration of $CO_2$ in the off-gas upon a considerable change in the acrolein concentration confirms the earlier conclusion (4) that the reaction of $CO_2$ formation from acrolein is of zero order. This conclusion is not contradicted by the observed approximately linear increase in the amount of decomposed labeled acrolein with increasing concentration of the latter in the feed gas. The obvious reason for this, with an unchanged acrolein content on the catalyst surface (zero order of the $CO_2$-formation reaction), is the corresponding increase in the fraction of labeled acrolein on the catalyst as its concentration in the gas increases.

**Experiments with labeled propylene.** Propylene labeled with radiocarbon was obtained by dehydration of labeled *n*-propanol-1-$C^{14}$ over alumina at 450° with subsequent purification from aldehyde, ether, and unreacted alcohol impurities. A feed gas of composition $C_3H_6 : O_2 : N_2 = 40 : 10 : 50$ was passed through a trap containing unlabeled acrolein, cooled to the corresponding temperature. The results of the experiments are given in Table 2.

**Table 2**

| Experiment Nos. | T-ra, °C | $CO_2$ content in the gas at the outlet, % | S. a. $CO_2$, pulse/min per mg $BaCO_3$ | Acrolein content in the gas at the outlet, % | S. a. acrolein, pulse/min per mg $BaCO_3$ | S. a. propylene, pulse/min per mg $BaCO_3$ | Film: amount of carbon, mg | Film: s. a., pulse/min per mg $BaCO_3$ |
|---|---|---|---|---|---|---|---|---|
| 8 | 340 | 0.9 | 57 | 0.7 | 35 | 172 | 4.8 | 400 |
| 9 | 346 | 0.8 | – | 0.54 | – | – | – | – |
| 10 | 356 | 3.6 | 56 | 0.85 | 47 | 190 | 8.7 | 275 |
| 11 | 343 | 1.8 | 61 | 0.74 | 54 | 138 | 5.7 | 320 |
| 12 | 340 | 1.3 | 180 | 0.7 | 32 | 1918 | – | – |
| 13 a* | 345 | 1.9 | 9 | 0.38 | 0 | – | – | – |
| 13 b* | 344 | 1.3 | 3 | 0.55 | 0 | – | 3.8 | 351 |

* In experiment No. 13 the products were collected and analyzed separately for each 20 min of the experiment: a –analytical data for the first 20 min.; b –for the next 20 min.

An interesting result of these experiments was the considerably higher specific radioactivity (s. a.) of the film compared with the specific radioactivity of the initial propylene. In experiments Nos. 8, 10, and 11, the s. a. of the film was, respectively, 2.3, 1.45, and 2.3 times greater than the s. a. of the initial propylene. The values found for the ratio of the s. a. of the film to the s. a. of $C_3H_6$ are close to those that could occur in the case of selective formation of the film from the terminal methylene groups of intermediate products in the synthesis of acrolein. In the absence of isomerization of the double bond in propylene under the conditions of its synthesis and of acrolein synthesis, the s.

a. of the film in the indicated case should have been 3 times greater than that of the initial propylene. In the case of complete isomerization of the double bond under the indicated conditions, with selective formation of the film, the s. a. of the latter should have exceeded the s. a. of $C_3H_6$ by a factor of 1.5.

The results obtained may be regarded as indicating the preferential formation of the film from the terminal methylene groups of inter-

intermediate products of acrolein synthesis and by possible isomerization of the double bond under the synthesis conditions.* Apparently, differences in the degree of isomerization of the double bond under the synthesis conditions explain the differences in the ratios of the specific radioactivities of the film and of propylene in experiments Nos. 8, 11, and in No. 10. The smaller value of the ratio of these quantities in experiment No. 10, carried out at 365°, compared with the same ratio in experiments Nos. 8 and 11, carried out at 340 and 343°, may be connected with a greater degree of isomerization of the double bond at the higher temperature.

To clarify the behavior of the organic film during the synthesis of acrolein, after experiment No. 12 with labeled propylene only the gases were pumped out at 400°, without subsequent burn-off of the film. In experiment No. 13 the initial gas mixture for the synthesis, without addition of acrolein or radioactive propylene, was fed onto the catalyst covered with a radioactive film. As follows from the radioactivity of the film found at the end of the experiment, after 40 min of the run 60% of its initial radioactivity remained in the film. At the beginning of the experiment, a more active participation of the film in oxidation processes was observed. Thus, during the first 20 min of the experiment, 33% of the radioactivity of the film passed into $CO_2$. The portion of the film that remained unoxidized after the first 20 min of the experiment possesses considerable reactivity. During the next 20 min of the experiment, only 6% of the initial radioactivity passed into $CO_2$, although the film present on the catalyst surface still retained 61% of the initial radioactivity. The results of experiment No. 13 indicate the nonuniformity of the organic film.

Thus, as a result of the work carried out by the tracer-atom method, it has been shown that oxidation of propylene to $CO_2$ on a copper catalyst under the conditions studied proceeds mainly according to a consecutive scheme. Acrolein is an intermediate product of deep oxidation and, under the synthesis conditions, is partly oxidized to $CO_2$ and $H_2O$. It has also been shown that the organic film on the catalyst surface under the conditions of acrolein synthesis is formed predominantly from propylene or from intermediate products of acrolein synthesis.

In conclusion, the authors express their sincere gratitude to L. Ya. Margolis for participating in the discussion of the results.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received

18 VII 1961

## CITED LITERATURE

1. O. V. Isaev, L. Ya. Margolis, S. Z. Roginskii, *ZhOKh*, **29**, 1522 (1959).
2. O. V. Isaev, L. Ya. Margolis, I. S. Sazonova, *DAN*, **129**, 141 (1959).
3. V. S. Belyusov, Ya. B. Gorokhovatskii, M. Ya. Rubinshtein, A. V. Gershingorin, *DAN*, **132**, 1125 (1960).
4. O. V. Isaev, L. Ya. Margolis, *Kinetics and Catalysis*, **1**, 2, 237 (1960).
5. *Syntheses of Organic Preparations*, collection, **1**, 1949, p. 17.

* Since the propylene was not analyzed for the content of difficult-to-remove radioactive impurities, the indicated conclusion is preliminary.

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

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