# Chemistry

N. I. Popova, B. V. Kabakova, F. A. Milman, E. E. Vermel

1964

SovietRxiv

## Abstract

## Full Text

## Chemistry

**N. I. Popova, B. V. Kabakova, F. A. Milman, E. E. Vermel**

# On Some Features of the Gas-Phase Oxidation of Hydrocarbons on Copper Catalysts

*(Presented by Academician B. A. Kazanskii, 28 XI 1963)*

Despite the considerable increase in interest in the study of the heterogeneous oxidation of hydrocarbons, there still exists only a small number of thoroughly developed processes of so-called "mild" oxidation, as a result of which valuable oxygen-containing organic compounds can be obtained. These are oxidation reactions of a few substances—for example, benzene and certain aliphatic hydrocarbons to maleic acid, ortho-xylene and naphthalene to phthalic acid—on vanadium catalysts; ethylene to ethylene oxide—on silver catalysts; propylene to acrolein—on copper and bismuth-molybdenum catalysts. Until very recently, no systematic study had been carried out of the transformations of various representatives of one or another class of organic substances, even on the principal "mild" oxidation catalysts listed above.

In the present work, the principal regularities of the oxidation of certain hydrocarbons and of one unsaturated halohydrocarbon—methallyl chloride—on copper catalysts supported on silica were studied. It should be noted that, in order to obtain satisfactory yields of oxygen-containing compounds, in most cases additives of oxides of heavy metals and their salts, quite specific for each process, were introduced into the copper catalyst. It was shown earlier (^1) that these additives do not affect the activation energy of the reaction of formation of carbonyl compounds, but do change the activation energy of the process of formation of carbon dioxide. The kinetics of oxidation of various unsaturated and aromatic hydrocarbons were studied in a flow system and on a thin layer of catalyst. Kinetic measurements were carried out in the absence of external and internal diffusion complications at low contact times (of the order of 0.3 sec and less).

Under these conditions, the parallel course of the main reactions of formation of aldehydes and carbon dioxide was observed, and a zero order of reaction with respect to the hydrocarbon and a first order with respect to oxygen was established (within certain concentrations of the starting substances). Analysis of the liquid oxidation products in all experiments was carried out by distillation on a rectification column with an efficiency of 60 theoretical plates; in the case of oxidation of butene-1—by the gas-liquid chromatography method. The gases were analyzed on a VTI apparatus.

For all reactions, the results of the investigations carried out are presented in Table 1. As is seen from Table 1, the copper catalyst, depending on the structure of the molecule being oxidized, brings about either "mild" or "deep" oxidation.

If the structure of the molecule of an unsaturated or aromatic hydrocarbon contains a methyl or methylene group conjugated with a double bond or an aromatic ring, then the main products of the reaction are unsaturated and aromatic carbonyl compounds (yield approximately 70% based on converted hydrocarbon), and the oxidation proceeds very selectively at such a methyl or methylene group without destruc-

**Table 1**

*Kinetic constants of reactions for the formation of carbonyl compounds (A) and carbon monoxide (B) in the oxidation of hydrocarbons on copper catalysts*

| Formula of the substance oxidized | Yield of reaction products per converted hydrocarbon, %, main | Yield of reaction products per converted hydrocarbon, %, by-products | A: $k_1 \cdot 10^{-2}$ (at 300°) | A: $\varepsilon \pm 1$, kcal/mol | A: $\lg k_0$ | B: $k_2 \cdot 10^{-1}$ (at 300°) | B: $\varepsilon \pm 2$, kcal/mol | B: $\lg k_0$ | Energy of the C–H bond in the methyl group (*), kcal/mol |
|---|---|---|---|---|---|---|---|---|---|
| $CH_2=CH_2$ *(3)* | $CO_2$; $H_2O$ 100.0 | Carbonyl compounds – traces | – | – | – | – | – | – | 104.0, C–H bond |
| $CH_2=CH-CH_3$ (1) | $CH_2=CH-CHO$ 72.0 | $CO_2$; $H_2O$ 20.0<br>$CH_2O$; $CH_3CHO$; $C_2H_5CHO$; $CH_3COCH_3$ 8.0 | 7.95 | 11 | 2.5 | 1.75 | 23 | 7.2 | 77.0 |
| $CH_2=C(CH_3)_2$ *(4)* | $CH_2=C(CH_3)CHO$ 72.0 | $CO_2$; $H_2O$ 20.0<br>$CH_2O$; $CH_3CHO$; $C_2H_5CHO$; $CH_2=CH-CHO$ 8.0 | – | 13 | 4.0 | – | 22.0 | 7.0 | 76.0 |

| Formula of the substance oxidized | Yield of reaction products per converted hydrocarbon, %, main | Yield of reaction products per converted hydrocarbon, %, by-products | A: $k_1 \cdot 10^{-2}$ (at 300°) | A: $\varepsilon \pm 1$, kcal/mol | A: $\lg k_0$ | B: $k_2 \cdot 10^{-1}$ (at 300°) | B: $\varepsilon \pm 2$, kcal/mol | B: $\lg k_0$ | Energy of the C–H bond in the methyl group (*), kcal/mol |
|---|---|---|---|---|---|---|---|---|---|
| $CH_2=CH-CH_2-CH_2-CH_3$ *oxidized at 320° | $CH_2=CH-CHO$<br>40.0 | $CO_2$; $H_2O$<br>20.0 $CH_3-CH=CH-CHO$<br>10.0 $CH_3-CH-CH_2$; $C_2H_5-CH-CH_2$ (epoxides)<br>30.0 $CH_3CHO$; $C_2H_5CHO$; $C_3H_7CHO$ | [illegible] | 18 | 5.2 | – | 24.0 | 10.1 | – |
| $CH_2=CH-CH_2-CH_2-CH_3$ *oxidized at 370° | $CH_2=CH-CHO$<br>50.0 | $CO_2$; $H_2O$<br>25.0 $CH_3CH=CH-CHO$<br>10.0 $CH_3CH-CH_2$; $C_2H_5-CH-CH_2$; $CH_3CHO$ (epoxides)<br>15.0 $C_2H_5CHO$; $C_3H_7CHO$ | [illegible] | 18 | 5.2 | – | 24.0 | 10.1 | – |
| $CH_2=C(CH_3)-CH=CH_2$ (5) | $CH_2=C(CHO)-CH=CH_2$<br>75.0 | $CO_2$; $H_2O$<br>25.0 $CH_3CHO$<br>traces | 0.15 | 11 | 2.3 | 2.73 | 23 | 7.0 | – |
| $CH_2=CH-CH=CH-CH_3$ (5) | $CH_2=CH-CH=CH-CHO$<br>75.0 | $CO_2$; $H_2O$<br>25.0 $CH_3CHO$<br>traces | 0.29 | 13 | 2.7 | 2.73 | 23 | 7.0 | – |
| $CH_3-CH=CH-CH=CH-CH_3$ | $CH_3-CH=CH-CH=CH-CHO$<br>71.3 | $CO_2$; $H_2O$<br>25.0 $CHO-CH=CH-CH=CH-CHO$<br>3.7 | 0.56 | 15 | 3.2 | 0.90 | 19 | 5.4 | – |
| $CH_2=C(CH_3)(CH_2Cl)$ | $CH_2=C(CH_2OH)(CH_2Cl)$<br>95.0 | $CO_2$; $H_2O$<br>5.0 | – | – | – | – | – | – | – |
| $C_6H_5CH_3$ | $C_6H_5CHO$<br>75.0 | $CO_2$; $H_2O$<br>25.0 | 0.32 | 12 | 2.1 | 0.81 | 22 | 6.3 | 77.5 |
| *m*-$C_6H_4(CH_3)_2$ | *m*-$C_6H_4(CH_3)CHO$<br>75.0 | $CO_2$; $H_2O$<br>25.0 | 0.61 | 12 | 2.6 | 1.35 | 20 | 5.9 | 77.5 |
| *n*-$C_6H_4(CH_3)_2$ | *n*-$C_6H_4(CH_3)CHO$<br>75.0 | $CO_2$; $H_2O$<br>25.0 | 0.50 | 10 | 2.4 | 1.50 | 21 | 6.0 | 75.0 |

| Formula of the substance oxidized | Yield of reaction products per converted hydrocarbon, %, main | Yield of reaction products per converted hydrocarbon, %, by-products | A: $k_1 \cdot 10^{-2}$ (at 300°) | A: $\varepsilon \pm 1$, kcal/mol | A: $\lg k_0$ | B: $k_2 \cdot 10^{-1}$ (at 300°) | B: $\varepsilon \pm 2$, kcal/mol | B: $\lg k_0$ | Energy of the C—H bond in the methyl group (*), kcal/mol |
|---|---|---|---|---|---|---|---|---|---|
| $o$-$C_6H_4(CH_3)_2$ | $o$-$C_6H_4(CH_3)CHO$ 75.0 | $CO_2$; $H_2O$ 25.0 | 0.41 | 9 | 2.1 | 1.46 | 20 | 5.6 | 74.0 |
| $C_6H_6$ | $CO_2$; $H_2O$ 100.0 | Carbonyl compounds — traces; acids — traces | — | — | — | 8.2 | — | — | 104.0, C—H bond |

* The substances were oxidized on a pure copper catalyst; the others, on modified copper catalysts.

of the rest of the molecule. In this case carbon dioxide proves to be the principal, and sometimes (see Table 1) the only, by-product (yield 20–25% based on converted hydrocarbon). In the absence of the above-mentioned groups (for example, in ethylene and benzene), products of complete combustion are formed predominantly. It is interesting that the stationary chemical composition of the catalyst, established in the course of oxidation, is also different in the oxidation of these two groups of hydrocarbons. In the case of "mild" oxidation it is a mixture of cupric oxide and cuprous oxide ([2]); in the case of "deep" oxidation, according to Shapovalova, Gorokhovatskii, and Rubanik ([3]), confirmed by our analyses, it is mainly cupric oxide (up to 95% CuO in the oxidation of benzene). As is seen from the data of Table 1, if the molecule has not one but two methyl groups conjugated with a double bond (isobutene, hexadiene-2,4, xylenes), oxidation of only one methyl group occurs, and the formation of dialdehydes is almost not observed. The nature and structure of the initial hydrocarbon also has a significant effect on the rates of oxidation, with aliphatic hydrocarbons

Fig. 1. Polarogram of the liquid oxidation products of butene-1 over a copper catalyst on silica gel. Background—LiCl

Figure 1: Fig. 1. Polarogram of the liquid oxidation products of butene-1 over a copper catalyst on silica gel. Background—LiCl

being oxidized at higher rates than aromatic ones.

**Fig. 1.** Polarogram of the liquid oxidation products of butene-1 over a copper catalyst on silica gel. Background—LiCl

In the case of oxidation of butene-1 the process proceeds less selectively; namely, along with the main reaction product—methyl vinyl ketone—crotonaldehyde and a considerable amount (25-40%) of other oxygen-containing compounds are formed. The latter are also formed to a small extent in the oxidation of propylene and isobutylene and, to an even lesser extent, in the oxidation of conjugated dienes. In the oxidation of benzene homologs, however, cleavage of the ring with formation of lower carbonyl compounds does not occur. The conversion of benzene over copper catalysts proceeds with great difficulty, and mainly $CO_2$ and $H_2O$ are formed.

It should be noted that the closeness of the values of the activation energies for the formation of carbonyl compounds is apparently due to the fact that the primary site of oxygen attack in the presence of a copper catalyst is the methyl or methylene groups of hydrocarbons located in the $\alpha$-position to a double bond or an aromatic ring, since the energies of the C—H bonds of these groups are close and differ by sufficiently low values (see Table 1).

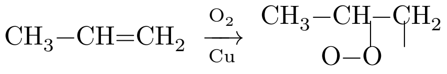
For benzene and ethylene the energies of the C—H bonds are comparatively high, which leads on copper contact to rupture of carbon-carbon bonds with their subsequent deep destruction.

Attention is drawn to the fact that the process of obtaining aldehydes over copper catalysts obeys the same regularities as the reactions of hydroperoxide formation during autoxidation and liquid-phase catalytic oxidation of hydrocarbons (7, 8), namely: insertion of the oxygen molecule occurs into the weakest C—H bond of the hydrocarbon molecule, without causing destruction of the molecule. If, however, the hydrocarbon molecule contains two C—H bonds with low and close bond-energy values, this insertion proceeds only at one of them with formation of a monohydroperoxide. This analogy makes it possible to assume that the result of the primary act of interaction of hydrocarbons with oxygen over copper catalysts is the formation of hydroperoxides with subsequent-

transformations of them into unsaturated carbonyl compounds on the surface of the catalyst:

$$CH_2{=}CH{-}CH_3 \xrightarrow[Cu]{O_2} CH_2{=}CH{-}CH_2OOH \xrightarrow{Cu} CH_2{=}CH{-}CHO - H_2O.$$

At the same time, apparently, the process of addition of the oxygen molecule at the double bond also takes place:



$$CH_3{-}CH{=}CH_2 \xrightarrow[Cu]{O_2} \underset{\quad O{-}O}{CH_3{-}CH{-}CH_2}$$

This second direction is the principal one in the chain gas-phase oxidation of olefins ($^9$), which is explained by the formation of more reactive molecular fragments; this subsequently leads to destruction of the molecules and to the formation of $CO_2$ and $H_2O$, as well as oxygen compounds of lower molecular weight.

The analysis carried out of the hydrocarbon oxidation process shows that the principal direction of attack by oxygen is determined both by the chemical composition of the catalyst and its modifying additives, and by the general structure of the molecule. Thus, for example, in the case of butene-1, attack at the methylene group is more hindered than at the methyl group (for example, in the case of propylene), apparently because of steric hindrance, which leads to intensification of the direction of attack at the double bond and, consequently, to a higher yield of unsaturated carbonyl compounds and other oxygen-containing products.

Since, in the opinion of Skirrow and Williams ($^{10}$), the activation energy of the process of oxygen addition at the double bond is lower than that at the methyl group, the reaction products at a higher temperature (370°) were found to contain a larger amount of unsaturated carbonyl compounds of the allylic type. In the oxidation of butene-1, one should expect the formation, as an intermediate product, of a more stable secondary hydroperoxide. Apparently, this circumstance can explain the fact that in this case, by applying the method of rapid freezing of the reaction products (to −80°) followed by distillation of the gases in vacuum, we were for the first time able qualitatively—iodometrically ($^{11}$) and polarographically (cf. Fig. 1 with polarograms of organic hydroperoxides according to the data of ($^{12}$))—to detect the presence of peroxide compounds in the products of oxidation of butene-1 on a copper catalyst. This fact supports the supposition expressed above concerning the formation of hydroperoxides as intermediate products in the oxidation of hydrocarbons on copper catalysts.

Institute of Petroleum and Coal-Chemical Synthesis
at Irkutsk State University

Received
27 XI 1963

## REFERENCES

[1] N. I. Popova, R. N. Stepanova, R. N. Stukova, *Kinetics and Catalysis*, **2**, 916 (1961). [2] N. I. Popova, E. E. Vermel, *Dokl. Akad. Nauk SSSR*, **124**, 842 (1959). [3] L. P. Shapovalova, Ya. B. Gorokhovatskii, M. Ya. Rubanik, *Ukr. Khim. Zh.*,

**28**, 1031 (1962). [4] N. I. Popova, A. Milman, *Izv. SO AN SSSR*, **59** (1962). [5] N. I. Popova, E. E. Vermel, F. A. Milman, *Kinetics and Catalysis*, **3**, 241 (1962). [6] M. Scwarz, *Chem. Rev.*, **47**, 75 (1950). [7] K. I. Ivanov, *Intermediate Products and Intermediate Reactions of the Autoxidation of Hydrocarbons*, 1949. [8] D. G. Knorre, Z. K. Maisus et al., *Usp. Khim.*, **26**, 416 (1957). [9] J. D. Mullen, G. Skirrow, *Proc. Roy. Soc.*, **244**, 312 (1958). [10] G. Skirrow, Q. Williams, *Proc. Roy. Soc.*, **268**, 537 (1962). [11] Kenzi C. Nozaki, *Ind. and Eng. Chem.*, **18**, 583 (1946). [12] N. V. Fok, A. B. Nalbandyan, in: *Problems of Chemical Kinetics, Catalysis, and Reactivity*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 222.

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

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