PHYSICAL CHEMISTRY

Academician A. A. BALANDIN, G. V. ISAGULYANTS, A. P. RUDENKO, and G. STEGER

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Academician A. A. BALANDIN, G. V. ISAGULYANTS, A. P. RUDENKO, and G. STEGER

RADIOCHEMICAL MEASUREMENT OF THE RATE OF CARBON FORMATION DURING THE DECOMPOSITION OF ETHYL ALCOHOL ON A DEHYDROGENATING CATALYST

In our previous works ([1,2]), investigations were reported of the mechanisms of resin and carbon formation during the decomposition of ethyl alcohol on catalysts, carried out on the basis of studying the reaction products and their rates of formation. It follows from these works that, in the decomposition of ethyl alcohol on a dehydrogenating catalyst, several mechanisms of carbon formation occur, depending on the temperature conditions. At 200–600° a low-temperature mechanism is observed, consisting in the polycondensation of acetaldehyde first formed from the alcohol; at higher temperatures, polycondensation of the original ethyl alcohol with unsaturated products of condensation into a carbonaceous substance becomes possible, as does the polycondensation of various hydrocarbons previously obtained from the decomposing alcohol.

In view of the complexity and multistage character of the processes of carbon formation, which could be studied mainly only from certain overall effects and indirect data, it was of interest to clarify the role of acetaldehyde and of alcohol as the starting material for carbon formation by measuring the rates of individual stages of this complex process, which makes it possible to use the isotope kinetic method of M. B. Neiman ([3,4]). This method was first applied to heterogeneous-catalytic reactions by A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isagulyants, A. P. Shcheglova, and E. I. Popov ([5]).

Radiochemical methods had previously been used to elucidate a number of questions concerning carbon formation during the decomposition of various organic substances ([6–10]). Thus, MacMahon ([7]) established by a radiochemical method that, at low temperatures of cracking of paraffin hydrocarbons, carbon is obtained at the expense of the carbon of the entire original molecule; A. A. Balandin and co-workers ([5,9]) showed that, in the dehydrogenation of a butane-butylene mixture, carbon is formed to the extent of 90% from divinyl and only 1.5% directly from butane; G. M. Zhabrova and B. M. Kadenatsi ([10]) found that, under conditions of obtaining divinyl from ethyl alcohol, carbon is formed mainly from the alcohol, etc.

In the present work, under the same conditions, two series of experiments were carried out: with pure ethyl alcohol and with a mixture of ethyl alcohol with 3% ^{14}C-labeled acetaldehyde (specific radioactivity 11,900 counts/mg $BaCO_3$ in 1 min). The experiments were carried out in a flow apparatus according to the procedure described earlier (^{1,2}), at 305 and 485°, with contact times of 1-9 sec, and on a copper-silica gel catalyst prepared according to (^{1}). In the experiments with addition of labeled acetaldehyde, the specific radioactivity of the carbonaceous substance obtained, acetaldehyde, and alcohol was measured according to the procedure (^{5}). The activity of the alcohol and carbon was determined in $BaCO_3$ targets after combustion of the samples. The activity of acetaldehyde was determined in targets of 2,4-dinitrophenylhydrazone, with the corresponding recalculation to the equivalent radioactivity of $BaCO_3$. The carbonaceous substance was burned in the same apparatus,

in which the main experiments were carried out, at 650° after removal of volatile organic substances.

Preliminary experiments with C^{14}-labeled ethylene and acetaldehyde showed that the rate of formation of carbonaceous substance from acetaldehyde is several times greater than from ethylene, since the percentage conversion of radiocarbon into carbonaceous substance from acetaldehyde is 3 times greater than in the case of ethylene. On the basis of these data we found it possible to use the following scheme for determining the individual rates of reactions in the conversion of ethyl alcohol into carbon, in which the role of ethylene in the carbon-formation process was neglected:

$$\begin{tikzcd}
C_2H_5OH \arrow[rr, shift left, "\omega_1"] \arrow[dr, "\omega_2"'] & & CH_3CHO \arrow[ll, shift left, "\omega_1'"] \arrow[dl, "\omega_3"] \\
& \text{carbon} &
\end{tikzcd}$$

Fig. 1. Effect of contact time on the course of decomposition of ethyl alcohol at a temperature of 305°.
1 –unreacted alcohol, 2 –hydrogen, 3 –carbonaceous substance calculated as free carbon, 4 –ethylene (all concentrations are given in millimoles per liter of gaseous products)

An analogous scheme was used by A. A. Balandin et al. to determine the individual rates of reactions in the dehydration of ethyl alcohol on aluminosilicates (^{11}).

As a result of the reactions proceeding in accordance with the scheme given, with rates ω_1, ω_1', ω_2, ω_3, the alcohol, acetaldehyde, and carbon will have specific radioactivities equal to α, β, and γ, respectively.

Solving the system of differential equations for the individual reaction rates and the corresponding equations for changes in radioactivity, as described previously ([11]), we obtain the following expressions for the individual rates of the process under study:

Fig. 2. Effect of contact time on the course of decomposition of ethyl alcohol at a temperature of 485°.
1 —unreacted alcohol, 2 —hydrogen, 3 —carbonaceous substance calculated as free carbon, 4 —ethylene (all concentrations are given in millimoles per liter of gaseous products)

$$\omega_1 = \frac{d\beta}{d\tau}\frac{C_2}{\alpha-\beta}, \tag{1}$$

$$\omega_1' = \frac{d\alpha}{d\tau}\frac{\alpha}{\beta-\alpha}, \tag{2}$$

$$\omega_2 = \frac{dC_3}{d\tau} - \omega_3, \tag{3}$$

$$\omega_3 = \frac{\dfrac{d\gamma}{dt} + \dfrac{dC_3}{d\tau}(\gamma-\alpha)}{\beta-\alpha}. \tag{4}$$

The data on the kinetics of decomposition of ethyl alcohol without additions of labeled acetaldehyde at 305 and 485° are given in Figs. 1 and 2. In these figures the ordinate axis gives the amount of substance in millimoles per liter

of the vapor of the initial alcohol; along the abscissa axis—the nominal contact time, defined as the reciprocal of the volumetric rate of vapor passage. In calculating these quantities, the change in volume (at N.T.P.) occurring during the reaction was taken into account (the mean value between the volumes at the reactor inlet and outlet was used). From the data obtained, by graphical

Fig. 3. Effect of contact time on the specific radioactivity of the decomposition products of ethyl alcohol with 3% labeled C^{14} acetaldehyde at a temperature of 305°. 1 —unreacted alcohol, 2 —acetaldehyde, 3 —carbonaceous substance (all specific activities are given as percentages of the initial value)

differentiation the quantities needed for calculations by formulas (1)—(4) were determined: C_2 (acetaldehyde concentration) and $\frac{dC_3}{d\tau}$ (total rate of carbon formation). The quantities of specific radioactivity needed for calculations by formulas (1)—

Fig. 4. Effect of contact time on the specific radioactivity of the decomposition products of ethyl alcohol with 3% labeled C^{14} acetaldehyde at a temperature of 485°. 1 —unreacted alcohol, 2 —acetaldehyde, 3 —carbonaceous substance (all specific activities are given as percentages of the initial value)

(4) were determined from the corresponding curves (see Figs. 3 and 4), and the derivatives were found by graphical differentiation. Table 1 gives the results of calculations by formulas (1)–

Table 1

Values of the individual rates of the process of decomposition of ethyl alcohol on a dehydrogenating catalyst at different temperatures and contact times, obtained by a radiochemical method

τ, sec	305°: w_1	305°: w_1'	305°: w_2	305°: w_3	485°: w_1	485°: w_1'	485°: w_2	485°: w_3
1	–	–	–	–	–	–	–	–
2	3.8	0.05	0.16	0.12	–	–	–	–
3	2.1	0.03	0.11	0.18	3.7	0.07	0.12	0.04
4	1.6	0.02	0.08	0.20	2.8	0.08	0.10	0.06
5	1.2	0.01	0.06	0.23	2.0	0.08	0.08	0.09
6	0.9	0.008	0.045	0.25	1.3	0.08	0.05	0.11
7	0.7	0.005	0.035	0.26	0.7	0.08	0.04	0.12
8	0.5	9.003	0.025	0.27	0.3	0.08	0.03	0.13
9	0.4	0.001	0.020	0.28	0.07	0.08	0.03	0.13

(4), expressed in mM/sec per liter of gaseous products. The use of data on the kinetics of decomposition of pure ethyl alcohol for calculating the radiochemical quantities obtained in experiments with a mixture of alcohol containing 3% acetaldehyde was entirely permissible, since in our work ([2]) it was shown that small additions of acetaldehyde to the mixture with alcohol do not affect the rate of carbon formation, and the effect becomes noticeable only at additions that raise the acetaldehyde concentration above its value corresponding to the depth of conversion under the given conditions.

Comparison of the obtained values of reaction rates at different contact times and two temperatures gave the following results. At 305°, increasing the contact time by a factor of 4 leads to a twofold increase in the rate of carbon formation from acetaldehyde; at the same time, a tenfold decrease is observed in the rate of carbon formation from alcohol and in the rate of formation of aldehyde from alcohol. The ratio of the rates of carbon formation from acetaldehyde and from alcohol thereby increases from 0.75 to 15, i.e., increases by a factor of 20. At 485°, a similar fourfold increase in contact time leads to a threefold increase in the rate of carbon formation from acetaldehyde, with a simultaneous fourfold decrease in the rate of carbon formation from alcohol and a fortyfold decrease in the rate of formation of aldehyde from alcohol. The ratio of the rates of carbon formation from aldehyde and from alcohol changes from 0.55 to 4.3, i.e., increases by a factor of 8.

The comparison carried out, revealing the direction of changes in the rates of the individual reactions with increasing contact time and temperature, shows that with increasing contact time there is a decrease in the rate of conversion of alcohol into carbon and of alcohol into acetaldehyde, and an increase in the rate of conversion of aldehyde into carbon; i.e., the share of participation of aldehyde in the carbon-formation process increases. For example, at a contact time of 9 sec. and a temperature of 305°, 94% of the carbonaceous substance is obtained from acetaldehyde and only 6% from alcohol. With increasing temperature, on the contrary, a decrease is observed in the share of participation of acetaldehyde in the carbon-formation process. For example, at 485° and a contact time of 9 sec., only 82% of the carbonaceous substance is obtained from acetaldehyde, and the remainder from alcohol.

Thus, by a radiochemical method, using C^{14}, it has been found that, in the decomposition of ethyl alcohol on a dehydrogenation catalyst in the temperature range 300-500°, the carbonaceous substance is formed mainly from acetaldehyde. The contribution of ethyl alcohol as the initial material in the carbon-formation process increases with increasing temperature, from 6% at 305° to 18% at 485° and a contact time of 9 sec.

The data obtained confirm the concept, expressed by us earlier ([1],[2]), of the active participation of acetaldehyde in the process of low-temperature carbon formation from ethyl alcohol, and the previously proposed scheme of the process of polycondensation of acetaldehyde into carbonaceous substance. In this scheme, preliminary dehydrogenation of the alcohol is a necessary condition for realization of the low-temperature mechanism of carbon formation.

The data obtained also confirm the correctness of the assumption that one of the pathways for high-temperature carbon formation during the decomposition of ethyl alcohol is the direct polycondensation of ethyl alcohol with unsaturated condensation products, leading to the formation of carbonaceous substance. The role of ethyl alcohol as the initial material of carbon formation indeed increases with increasing temperature.

Moscow State University
named after M. V. Lomonosov

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
26 XII 1959

REFERENCES CITED

1. G. Stegner, A. A. Balandin, A. P. Rudenko, *Izv. AN SSSR, OKhN*, 1959, No. 11, 1896.

2. G. Stegner, A. A. Balandin, A. P. Rudenko, *Izv. AN SSSR, OKhN*, 1960, No. 1, 24.

3. M. B. Neiman, *ZhFKh*, **28**, 1235 (1954).

4. M. B. Neiman and A. F. Lukovnikov, Chain Reactions of Oxidation of Hydrocarbons in the Gas Phase, Collection, Publishing House of the Academy of Sciences of the USSR, 1955.

5. A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isagulyants, A. P. Shcheglova, and E. I. Popov, *Izv. AN SSSR, OKhN*, 1957, 165.

6. R. W. Blue, C. J. Engle, *Ind. and Eng. Chem.*, **43**, 494 (1951).

7. R. E. McMahn, *Ing. and Eng. Chem.*, **47**, 844 (1955).

8. M. M. Sakharov, Study of Catalytic Cracking Reactions of Hydrocarbons Using Radiocarbon C^{14}, Candidate dissertation, Moscow, 1955.

9. A. A. Balandin, M. B. Neiman, O. K. Bogdanova, G. V. Isagulyants, A. P. Shcheglova, and E. I. Popov, *Izv. AN SSSR, OKhN*, 1957, 270.

10. G. M. Zhabrova, B. M. Kadenatsi, *Problems of Kinetics and Catalysis*, **9**, 187 (1957).

11. A. A. Balandin, G. V. Isagulyants et al., *Izv. AN SSSR, OKhN*, 1958, No. 2, 233.

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

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