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O. M. Vinogradova, N. P. Keier

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Abstract

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O. M. Vinogradova, N. P. Keier
and Corresponding Member of the Academy of Sciences of the USSR
S. Z. Roginskii

Investigation of the Mechanism of Divinyl Synthesis by the S. V. Lebedev Method Using Radioactive Carbon

To explain the mechanism of formation of divinyl from ethyl alcohol, various schemes have been proposed (1-6). At present, the best substantiated scheme for the formation of divinyl from ethyl alcohol may be considered to be the one proposed by Yu. A. Gorin (4) and, independently of him, by M. Ya. Kagan and co-workers (5). According to this scheme it is assumed that the formation of divinyl from ethyl alcohol proceeds in 4 stages:

1) $2C_2H_5OH \rightarrow 2CH_3CHO + 2H_2$
2) $2CH_3CHO \rightleftarrows CH_3{-}CHOH{-}CH_2{-}CHO \rightarrow CH_3{-}CH{=}CH{-}CHO + H_2O$
3) $CH_3{-}CH{=}CH{-}CHO + C_2H_5OH \rightleftarrows CH_3{-}CH{=}CH{-}CH_2OH + CH_3CHO$
4) $CH_3{-}CH{=}CH{-}CH_2OH \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O$

American scientists—Quattlebaum, Toussaint, and others (6)—arrived at similar conclusions. However, they believe that the conversion of crotonaldehyde into divinyl occurs in a single stage by deoxygenation, which presupposes adsorption of crotonaldehyde in the enolic form, redistribution of hydrogen between the adsorbed molecules of ethyl alcohol and crotonaldehyde, and desorption of the latter in the form of divinyl, leaving oxygen on the catalyst.

In the present work, an attempt was made to clarify the stepwise mechanism of the formation of divinyl from ethyl alcohol with the aid of molecules labeled with radioactive carbon.

1. Reaction in the layer. The transformations of ethyl alcohol and aldehydes in the adsorption layer were first studied. For this purpose, ethyl alcohol was adsorbed at room temperature on the Lebedev catalyst; then, as the temperature was raised to 500°, desorption of the volatile reaction products was carried out. The latter were separated by distillation in vacuum and identified from the dependence of vapor pressure on temperature.

In this way it was shown that, in the adsorption layer on the Lebedev catalyst, ethyl alcohol is converted into ethylene and acetaldehyde and, in small amounts, into diethyl ether. Divinyl was not detected under these conditions.

A study carried out in an analogous manner on the transformations of acetaldehyde showed that, in the adsorption layer on the Lebedev catalyst, it is converted mainly into crotonaldehyde and higher condensation products; moreover, the formation of crotonaldehyde was observed already at room temperature. Ethylene and insignificant amounts of divinyl are formed simultaneously.

A study of the transformations of crotonaldehyde showed that it is converted into higher condensation products, ethylene, and divinyl. A slight formation of acetaldehyde was also observed. The introduction into the adsorption layer of small amounts of ethyl alcohol during the study of aldehyde adsorption increases the yield of divinyl both from acetaldehyde and from crotonaldehyde.

The data presented show the possibility of the following sequence of transformations in the adsorption layer: ethyl alcohol —acetaldehyde —crotonaldehyde —divinyl. This confirms the possibility of divinyl formation according to the Gorin–Kagan scheme, but does not prove that this route is the principal one.

2. Study of genetic relationships by means of labeled molecules

Table 1

Initial radioactive substance and its specific radioactivity, imp. per 1 mg $BaCO_3$	Specific radioactivity of reaction products: ethyl alcohol	Specific radioactivity of reaction products: acetaldehyde	Conversion of H, %
Ethyl alcohol 469	373	320	98
Ethyl alcohol 272	214	206	98
Acetaldehyde 280	47	45	100

By adding, during synthesis, C^{14}-labeled substances to the initial ethyl alcohol, whose role in the process is of interest to us, and by studying the distribution of C^{14} in the synthesis products, it is possible to establish the mutual transformations of various substances in the reaction and the extent of their participation in the formation of divinyl. This makes it possible to establish the main route of divinyl formation and to determine the contribution of other processes to its synthesis.

The investigation was carried out in a dynamic apparatus of small size. From the synthesis products, ethyl alcohol, acetaldehyde, ethylene, diethyl ether, and divinyl were isolated and analyzed for C^{14} content.

3. Isotopic exchange of alcohol with aldehyde

A study carried out with mixtures of labeled ethyl alcohol and acetaldehyde showed that, in the condensate obtained as a result of synthesis, ethyl alcohol, acetaldehyde, and divinyl have similar specific radioactivities. This value is considerably lower than the specific radioactivity of the initial ethyl alcohol (Table 1).

In experiments carried out with mixtures of C^{14}-labeled acetaldehyde with ethyl alcohol, we again obtained ethyl alcohol and acetaldehyde with similar specific radioactivities, lower than the specific radioactivity of the initial acetaldehyde.

Table 2

Catalyst	Temperature, °C	Contact time	Conversion of H, %
Lebedev	300	4–8 sec.	90
Lebedev	200	the same	83
Lebedev	21	1 hr.	60
Al_2O_3	390	4–8 sec.	98
ZnO	390	the same	23
Without catalyst	21	24 hr.	0*
Without catalyst	21	2 mo.	58*

* In a liquid mixture of ethyl alcohol with labeled acetaldehyde (10%).

The redistribution of radioactivity between acetaldehyde and ethyl alcohol observed by us on the Lebedev catalyst is a consequence of the redistribution of hydrogen between these two molecules. This redistribution leads to an apparent redistribution of radioactive carbon. This is a curious example of intermolecular isotopic exchange of one element that is a direct consequence of an ordinary chemical reaction involving migration of another element.

The closeness of the specific radioactivities of acetaldehyde, alcohol, and divinyl obtained in these experiments indicates that this process occurs at a rate considerably exceeding the rate of divinyl formation. Divinyl is formed from a mixture of alcohol with aldehyde in which the isotopic exchange of carbon through hydrogen redistribution has in fact already been completed.

The rate of this process can conventionally be characterized by the percentage of hydrogen redistribution, expressing the ratio of the specific radioactivity of the alcohol obtained to that specific radioactivity which would have resulted from equal distribution of all the radioactive carbon among all carbon-containing substances.

The study of the redistribution of hydrogen at different temperatures showed that its rate decreases slowly with decreasing temperature, remaining appreciable even at room temperature (Table 2). To elucidate the mechanism of this process, it was studied on typical dehydrogenating (ZnO) and dehydrating (Al_2O_3) contacts. It turned out that on Al_2O_3 the redistribution of hydrogen proceeds almost completely in the time during which, on the dehydrogenating contact, the exchange reaches only 23% (Table 2). This makes it probable that the process of hydrogen redistribution has no common stages with the process of alcohol dehydrogenation. Hydrogen redistribution also takes place without a catalyst, but at a very low rate. Thus, after the mixture had stood for 2 months, it reached only 58%. In other words, the Lebedev catalyst at 21° accelerates the isotopic exchange of C_2H_5OH with C_2H_4O by approximately 1500 times.

The interaction of acetaldehyde and ethyl alcohol may serve as a model reaction for the interaction of other alcohols and aldehydes in the Lebedev process. When transferred to the system crotonaldehyde–ethyl alcohol, the redistribution of hydrogen must inevitably lead to the formation of crotyl alcohol, which argues in favor of the scheme for the conversion of crotonaldehyde into divinyl according to Gorin–Kagan and is difficult to reconcile with the deoxygenation mechanism of Kvasbaum, Toussaint, and others. It is natural to think that if deoxygenation takes place for the system crotonaldehyde–ethyl alcohol, it should also take place for the system labeled acetaldehyde–ethyl alcohol. This would lead to the formation of radioactive ethylene from labeled acetaldehyde, i.e., the redistribution of C^{14} between acetaldehyde and ethyl alcohol, which we observed experimentally, would not occur.

4. Study of the role of crotonaldehyde. The synthesis of divinyl from a mixture of ethyl alcohol with labeled crotonaldehyde on the Lebedev catalyst leads to the production of divinyl whose specific radioactivity is considerably lower than the specific radioactivity of the initial crotonaldehyde. The presence of radioactivity in the divinyl unambiguously indicates that, in the course of the synthesis, crotonaldehyde is converted into divinyl.

The specific radioactivity of divinyl, reduced in comparison with the radioactivity of the initial crotonaldehyde, is a consequence of its dilution with inactive divinyl formed from ethyl alcohol. The role of crotonaldehyde in the formation of inactive divinyl from the alcohol could have been clarified from the specific radioactivity of crotonaldehyde isolated from the reaction products. However, we were unable to detect crotonaldehyde in the reaction products, which indicates the ease of its transformations on the Lebedev catalyst. Taking into account the results of experiments on the conversion of acetaldehyde in the adsorption layer, one may consider that the formation of crotonaldehyde from acetaldehyde proceeds at a high rate. This, as well as the fact that the rate of conversion of crotonaldehyde into divinyl, calculated from the radioactivity, exceeds the rate of conversion of ethyl alcohol into divinyl, speaks in favor of the intermediate formation of crotonaldehyde in the preparation of divinyl from ethanol.

The investigation carried out showed that, in the main, divinyl formation proceeds through the condensation of acetaldehyde to crotonaldehyde, which, in the presence of an excess of ethyl alcohol, as a result of hydrogen redistribution is converted into crotyl alcohol. Dehydration of the latter leads to the formation of divinyl. The use of the labeled-atom method made it possible to study hydrogen redistribution more thoroughly. This process apparently occurs through the formation and decomposition of an intermediate complex of alcohol and aldehyde molecules.

Thus, the principal sequence of stages of the Gorin—Kagan scheme is confirmed. What remains unclear is the nature of the participation in the pro-

in the process of ether and ethylene contained in the reaction products. The results obtained on this question are briefly presented in paper ([7]).

Institute of Physical Chemistry
Academy of Sciences of the USSR

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