Corresponding Member of the Academy of Sciences of the USSR S. Z. Roginskii, M. I. Yanovskii, G. M. Zhabrova, O. M. Vinogradova, B. M. Kadenatsi, and Z. A. Markova

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CATALYTIC SYNTHESIS OF UNSATURATED HYDROCARBONS OF THE C_4 SERIES LABELED WITH RADIOCARBON C^{14}, USING VAPOR-PHASE DISTRIBUTION RADIOCHROMATOGRAPHY

The broad use of labeled substances in various branches of science and technology is hindered by the insufficient development of work on methods for the synthesis of compounds of unusual isotopic composition. Often the preparation of these substances constitutes the main difficulty in setting up an experimental investigation.

As was pointed out by one of us (^{1}), the widespread opinion is incorrect according to which, in the synthesis of compounds of unusual isotopic composition, all problems can be solved by direct repetition of the techniques and methods of ordinary synthetic chemistry. It is often necessary to take into account the presence of intermolecular isotopic exchange, which causes a decrease in the content of the labeling isotope in the target product. An important factor is also the relatively high cost of most isotopes and the desirability of reducing to a minimum the losses and making the fullest possible use of the labeled substance. All these circumstances compel one to avoid the use of the most cumbersome techniques of ordinary synthetic chemistry and make it natural to seek typical simplified procedures, applying more widely the rich possibilities of heterogeneous catalysis, which make it possible finely to regulate the direction and depth of the desired reaction.

In the present work the results are presented of obtaining labeled unsaturated hydrocarbons from ethyl alcohol labeled with radiocarbon C^{14}. A distinctive feature of the method described is that all labeled molecules are obtained simultaneously as the result of a single catalytic process occurring on the catalyst for divinyl synthesis according to S. V. Lebedev, bypassing the lengthy and complex stages accepted for obtaining these substances in ordinary synthetic chemistry.

This work is a particular case of the general principle of synthesis of labeled molecules (^{1}), which consists in carrying out a group synthesis leading to the

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production of a mixture of a series of substances with unusual isotopic composition, followed by the application of physicochemical separation methods that make it possible to isolate the labeled substances in the individual state.

Of special interest was the isolation of labeled hydrocarbons of the C_4 series with different degrees of unsaturation and in different structural-isomeric forms, characterized by very close boiling points. Such hydrocarbons were butadiene (divinyl) with b.p. 4.5°; α-butylene with b.p. 6.3°; β-butylene (cis form) with b.p. +3.64°; β-butylene (trans form) with b.p. +0.86°.

Carrying out the catalytic synthesis

The catalytic synthesis was carried out on S. V. Lebedev' s catalyst (^{2}), at 390°, in an ordinary dynamic apparatus, a description of which is given earlier (^{5}). For the synthesis, labeled ethyl alcohol $C^{14}H_3C^{14}H_2OH$ with spe–

with a specific radioactivity of 0.724 Ci/ml. Since the purpose of this study was not to isolate products with maximum specific activity, for convenience in work the labeled radioactive alcohol was diluted in individual experiments from 5 to 40 times.

Chromatographic separation of gaseous labeled products. Chemical and radiochemical analysis and separation of gaseous radioactive products were carried out on a gas radiochromatograph, the description and operating principle of which are given in the work (^{3}). The instrument is a combination of an ordinary gas–liquid or vapor-phase chromatograph with an attachment for simultaneous continuous recording of the radioactivity and concentration of vapors (or gases) leaving the chromatographic column. Recording of the vapor content in the carrier-gas stream (nitrogen or hydrogen) was performed with an ordinary thermoconductometric

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Fig. 3. Chromatograms of a mixture of hydrocarbons during their successive separation. a—initial chromatogram, b—chromatogram of the separated α- and β-cis-C4H8, c—chromatogram of the separated β-trans-C4H8 and divinyl.

Figure 3: Fig. 3. Chromatograms of a mixture of hydrocarbons during their successive separation. a—initial chromatogram, b—chromatogram of the separated α- and β-cis-C4H8, c—chromatogram of the separated β-trans-C4H8 and divinyl.

gas analyzer. For recording radioactivity, a flow-through radiometric cuvette was used, with two thin-walled end-window counters ([4]) mounted in it (window thickness 0.8-1 mg/cm^2), connected

connected into the counting-rate meter circuit, with six ranges of 200, 600, 2000, 6000, 20,000, and 60,000 pulses/min. The readings of the gas analyzer and of the counting-rate meter are recorded simultaneously on the tape of an EPP-09 multiposition electronic potentiometer with ranges of 5 mV and 10 mV.

Fig. 3. Chromatograms of a mixture of hydrocarbons during their successive separation. **a**—initial chromatogram, **b**—chromatogram of the separated α- and β-cis-C_4H_8, **c**—chromatogram of the separated β-trans-C_4H_8 and divinyl.

Figure 1 presents a typical chromatogram of a mixture of gaseous radioactive products of divinyl synthesis by the method of S. V. Lebedev from labeled alcohol ($C_2^{14}H_5^{14}OH$) on one of the catalyst samples. The chromatogram consists of two curves. The lower curve is a record of activity, and the upper one is a record of the concentration of substances at the outlet from the column. It is easy to show (4) that the specific radioactivity of any component is, at a certain selected scale, the ratio of the areas under the peaks corresponding to this substance on the left and right curves of the chromatogram.

The radiochromatogram shows that, under the experimental conditions, the principal gaseous product is divinyl (81.3%). The content of butylenes does not exceed 4.7%.

By heat treatment of the catalyst and by introducing additives, it is possible to change the ratio of products, as is shown in the chromatogram (Fig. 2), taken after synthesis on a carbonized catalyst. As follows from Fig. 2, in this case the bulk of the gaseous products consists of butylenes (51%), while the divinyl content does not exceed 25%. The increase in the butylene content is connected with hydrogenation of divinyl on the coked catalyst (5). Saturated hydrocarbons (butane) also appear in the gas.

It is characteristic that the specific activities of the hydrocarbons (in pulses/min$\cdot$cm^3) presented in the chromatograms of Figs. 1 and 2 are approximately identical. The gas mixture obtained on the carbonized catalyst was subjected to chromatographic separation. At the time marked on the chromatogram by point *A* (Fig. 3a), the gas stream leaving the column was directed into a trap with

Fig. 4. Absorption spectra of butylenes. a —fraction I, b —fraction II, c —fraction III. Cuvette thickness 20 cm

Figure 4: Fig. 4. Absorption spectra of butylenes. a —fraction I, b —fraction II, c —fraction III. Cuvette thickness 20 cm

liquid air. Freezing out of α-C_4H_8 was continued up to point B, after which the gas was directed past the trap into the exhaust system. At the moment corresponding to B, the gas was directed into a second trap, in which freezing out of β-trans-C_4H_8 was continued until the moment corresponding to Γ. In exactly the same way the fractions β-cis-C_4H_8 and C_4H_6 were frozen out (D, E, Zh, Z). To verify the chemical and radiochemical purity of the isolated substances, the fractions α-C_4H_8 and β-cis-C_4H_8 were thawed and again passed into the chromatographic column for repeated radiochromatography. The resulting radiochromatogram is shown in Fig. 3b. A comparison of Figs. 3a and 3b shows that α-C_4H_8 and β-cis-C_4H_8 from chromatogram 3a were transferred to chromatogram 3b in pure form, without admixture of neighboring fractions. In an analogous manner, the fractions β-trans-C_4H_8 and C_4H_6 were transferred (Fig. 3c).

For the identification of the individual fractions, their infrared absorption spectra were recorded. The absorption spectra were obtained on an IKS-1 spectrograph in the region 2–15 μm, which includes the frequencies of deformation vibrations of C—H bonds and stretching vibrations of C=C and

C–C bonds. The position of the absorption bands corresponding to these frequencies is associated with the existence of definite groupings of atoms in the butylene molecule and could serve as an indication of the presence of one or another isomer.

The absorption spectra of the individual fractions are presented in Fig. 4. In accordance with literature data (^{7}), the first fraction should be assigned to α-butylene, the second to β-trans-butylene, and the third to β-cis-butylene. In our study, natural varieties of silica gel (diatomite, infusorial earth, etc.) impregnated with nitrobenzene were used as the stationary phase (40 g of nitrobenzene per 100 g of sorbent).

Promising is the combination of chromatography with rectification, extraction, and countercurrent distribution. These methods possess much greater productivity and can be used for preliminary group separation of the mixture into a series of fractions, followed by isolation of the individual components.

The results presented for the synthesis of labeled divinyl and butylenes illustrate, as it seems to us, the simplicity and convenience of the method. The catalytic experiment lasts about 1 hour, and the chromatographic separation takes 2–2.5 hours. Thus, in 3–4 hours it is possible to obtain four radiochemically pure products, the synthesis and isolation in pure form of which by the usual route would take several days.

Fig. 4. Absorption spectra of butylenes. *a* –fraction I, *b* –fraction II, *c* – fraction III. Cuvette thickness 20 cm.

Great possibilities for the preparation of various compounds labeled with C^{14} are opened up by the hydrogenation of CO according to Orlov–Fischer–Tropsch, the synthol process (^{1}), and hydrocondensation according to Eidus (^{8}) and Zelinsky (^{9}).

Institute of Physical Chemistry
Academy of Sciences of the USSR

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