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Parent hydrocarbon determination by means of gas chromatography

During recent years gas chromatography (GC) has even been favoured as a method for solving problems concerning the constitution of organic compounds. Particularly, its use as a fingerprint determination of a compound enabling one to gain very rapid and reliable information with respect to the character of a given sample is possible.

Among the many methods used for determining the carbon structure in classical organic analysis, there are two methods which especially are suitable for adaptation in the form of reaction GC:

(1) the mild, but not in the least universal, method of catalytic hydrogenation;

(2) a more universal but not fully unambiguous (with respect to reaction products) reduction method by means of zinc dust.

The first method was used by BEROZA[1] who hydrogenated the substance on Pt-group metals, reduced on some suitable support, in an electrically heated aluminium tube.

We have used the second method based on a method of VON BAEYER[2] which is more than a hundred years old and which has also been modified for the submicro scale[3]. GASPARIČ[5] has used CLAR's low-temperature modification[4] of this method in connection with paper chromatography for the study of the constitution.

In this study a TPGC apparatus, manufactured by Development Laboratories and Workshops in Olomouc, and equipped with a TC detector, was used. The dual coiled column system was filled with 20% Apiezon L–Chezasorb. In front of the packed column was inserted a reactor[8] made of Supremax glass filled with a mixture of distilled zinc dust (min. 99.9%) and diatomaceous support; this was heated with a resistance oven forming the outer shell of the reactor tube. The sample was introduced into the reactor by means of a microsyringe. Hydrogen was used as carrier gas. The substances leaving the column were identified on the basis of their retention times as well as by chemical reactions[6].

It was found that under similar conditions, aliphatic as well as aromatic halogen derivatives, and alcohols, aldehydes and ketones of all classes are quantitatively converted into their corresponding parent hydrocarbons. With substances containing other functional groups, no uniform conversion takes place under the conditions mentioned below and therefore these groups are the object of a further study.

In order to obtain a quantitative conversion the following parameters have proved to be critical.

The reactor temperature

The optimum working temperature is near the melting point of zinc (from 410 to 420°). In the case where the zinc is deposited in greater amounts on the diatomaceous support one can work with even higher temperatures. It is sometimes very convenient to use higher temperature because with such temperatures melting takes place and results in the renovation of the zinc surface. It has already been proved

that the conversion in the exhausted reactor can be increased by extending the time interval between individual doses.

Flow rate of the carrier gas

The conversion increases with decreasing flow rate (longer retention time of a sample in the reactor, thus greater chance of establishing perfect thermodynamic equilibrium). A flow rate of 20 ml H_2/min was chosen as optimum.

The amount of the sample and the quantity of zinc in the reactor

It was found that the degree of conversion depends on the ratio between the amount of sample and the amount of zinc in the reactor (and thus the dimensions of the reactor). In this case for the conversion with the groups of substances already mentioned to be quantitative, the other given optimum conditions must be fulfilled and it is necessary that the reactor contains a 7×10^4 greater amount of zinc than would be necessary as a minimum to induce quantitative reduction. With such an increase in the size of the reactor the gas hold space also increases which results in an extension of the peak width. For 5-μl doses, which were chosen with respect to their reproducibility and the possibility of quantitative evaluation of the degree of conversion (planimetry of the peak areas), a reactor of the size 20 × 2.2 cm proved to be best. With this reactor 100% conversion still takes place after the introduction of several tens of 5 μl samples and the introduction of several thousand 0.1–0.2 μl samples (for qualitative studies).

Quality of the zinc support

The choice of the reactor packing is influenced by the high cracking efficiency of some supports[7]. The use of the 40% (w/w) Zn/Chezasorb packing of the reactor at 424° resulted, even with chlorobenzene (from which benzene is developed and characterized by its appreciable stability), in the formation of 3–5% of pyrolysis products in addition to 95–97% of benzene. The pyrolysis products only disappear from the chromatogram when the chlorobenzene conversion ceases to be quantitative. With the use of Chromaton N (a product of Lachema) the formation of low-molecular cracking fragments was depressed. Even the glass walls of the reactor show some slight pyrolytic and reaction activity[7,8].

Thus a cylindrical glass reactor (20 × 2.2 cm) filled with 90% Zn/Chromaton N (w/w) at 420° and with a flow rate of 20 ml/min proved to give the best results.

In addition to the usual advantages of GC the method investigated has the following ones:

(1) The reactor packing is easily prepared and the life-time of the reserve packing is unlimited.

(2) The packing is insensitive to catalyst inhibitors. The zinc need not be activated and any hydrogen which is adsorbed in the packing plays no active role in the reaction.

(3) Low-molecular weight reactive fragments (H_2O, H_2S, HX) are intercepted in the reactor, thus preventing corrosion of the column and the detector. Water is retained in the reactor at temperatures above 350°. In this way a promising method

for the analysis of aqueous solutions of ethereal oils and essences and dilute aqueous solutions in general is suggested.

(4) There is the possibility of using larger samples for subsequent spectroscopic analysis.

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