Quantitative Hydrogenation of Unsaturated Hydrocarbons Isolated by Gas Chromatography

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A method is described for the quantitative hydrogenation of small amounts of unsaturated hydrocarbons isolated by gas chromatography. The application of the method to the identification of various types of unsaturated hydrocarbons is discussed.

Recently a qualitative hydrogenation method, developed for the purpose of identifying various types of unsaturated hydrocarbons isolated by gas chromatography, on the basis of the resulting hydrogenation products, was described by one of the present authors [1]. This method has proved to be of considerable value at this laboratory for solving identification problems related to unsaturated hydrocarbons. In certain instances, however, the need for a quantitative hydrogenation method arose. On that account the present method was developed and applied to a number of unsaturated hydrocarbons of various types. In the following, the method will be described and the results of the hydrogenations performed discussed in some detail.

EXPERIMENTAL

Condensation of the sample from the chromatograph. The method used has to be adapted to the boiling point of the sample. In the case of compounds boiling above about 60°C the sample was condensed in a narrow freezing trap of the cold-finger type, cooled in a dry ice-acetone bath. From the trap, the sample was transferred to a weighed capillary, sealed at one end, by means of a small syringe or it was sucked up directly into a weighed, open capillary. The capillaries were sealed and again weighed. In the case of somewhat higher-boiling liquids (above 80°C) it was also possible to condense the substance, in good yield, directly into a cooled, open capillary, which was attached to the outlet of the chromatograph by means of a glass tube, drawn out at one end to fit the diameter of the capillary.

For liquids boiling below about 60°C the yield was often not satisfactory when using the above methods and a dry ice-acetone bath. In that case a method, based on the principle of the cold wall, was used instead. The sample was condensed in a dry ice-acetone cooled, slightly curved tube filled with small glass beads, preferably not coarser than 60 mesh. A weighed capillary, one end of which was sealed, was attached to the narrow end of the tube and the other end was closed. The tube was then fastened in a cork, fitting
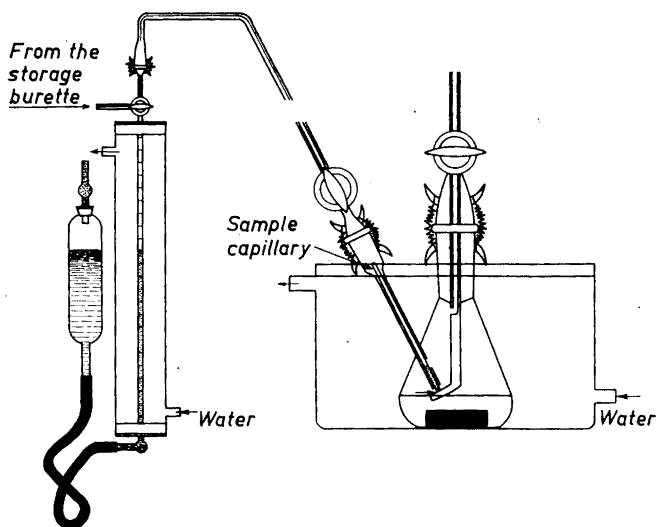
Fig. 1. Hydrogenation apparatus.

the opening of a Dewar flask. The Dewar flask was filled with dry ice-acetone to the proper height, and the cork inserted, so that the capillary was immersed into the cooling bath to about 3/4 of its length. After about 15 h most of the sample had been transferred to the capillary which was removed from the Dewar flask, sealed and weighed.

Hydrogenation apparatus. The hydrogenation apparatus used in the present work is shown in Fig. 1. It consisted of a 25 ml storage burette for hydrogen (not shown in the figure), a 5 ml measuring burette for hydrogen, a hydrogenation flask and connections between these parts. The two burettes were jacketed and the hydrogenation flask immersed in a bath. During the hydrogenation water of 20.0°C was pumped through the jackets and the bath. Mercury was used as sealing liquids in the burettes.

The hydrogenation flask consisted of a 25 ml Erlenmeyer flask with a B 14 neck. A capillary glass tube with a B 10 ground joint at the upper end was led through the side of the flask. This tube served as an inlet for the hydrogen and through it the sample-capillary was also introduced. An outlet for the hydrogen from the hydrogenation flask was provided through a hole in the tube leading through the neck of the flask. The lower end of this tube was curved, sealed and flattened, the reason for which will be mentioned later.

Hydrogenation procedure. Dioxane (6 — 8 ml) and platinum dioxide (Adam's catalyst, about 30 mg *) were filled into the hydrogenation flask, and the sample-capillary was introduced through the side tube. The lower end of the capillary should rest against the flattened part of the curved tube (*cf.* Fig. 1) and not against the bottom of the flask. In the latter case the Teflon-sealed stirring bar on the bottom of the flask would be hindered in its circular motion during the hydrogenation of the catalyst and there is also the danger of the capillary being crushed. The parts of the hydrogenation apparatus were connected, the burettes filled with mercury by raising the level of the mercury bottle and dry nitrogen was blown through the apparatus for about 10 min in order to expel the air followed by hydrogen for another 10 min.

The stopcock on the outlet tube of the hydrogenation flask was closed, the storage burette filled with hydrogen and then the valve on the hydrogen container closed. Water

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* A fairly large amount of catalyst was taken to ensure a rapid hydrogenation of the sample. It is recommended that the catalyst be changed between each run, since its activity decreases rather rapidly.

of 20.0°C was pumped through the burette jackets and the bath. After filling the measuring burette with hydrogen the connection between the two burettes was closed, the stirrer started and the catalyst hydrogenated. When no more hydrogen was absorbed (after about 1 h) more hydrogen was transferred from the storage to the measuring burette.

The mercury level in the latter was read, the magnet stirrer stopped and the sample capillary dropped to the bottom of the hydrogenation flask by turning the stopper of the latter. The sample capillary now rested with its lower end at the bottom of the hydrogenation flask while its upper end was supported by the capillary tube. By turning the stopper once more the sample capillary was broken. The stirrer was then restarted. The breaking of the capillary should take place beneath the surface of the solvent and it is essential that it during the continued stirring is more fully crushed in order that no sample is trapped within it. On this account, the capillary should be thinwalled and preferably not too narrow.

The uptake of hydrogen was followed. During the first 10 min of the hydrogenation the mercury level in the measuring burette was read every second minute and after that every fifth minute. The stopcock on the inlet tube of the hydrogenation flask was closed whenever a reading was taken. When no change in the mercury level could be registered during two consecutive readings the hydrogenation was considered to be completed.

The equiv. weight E (weight equivalent to one double bond) was calculated from the formula

$$E = \frac{22412 \cdot 760 \, (273.2 + t) \cdot a}{273.2 \cdot V \cdot p} \qquad (1)$$

where:

a = the sample weight in g,
t = the temperature in °C,
p = the air pressure in mm Hg,*
V = the volume of hydrogen consumed in ml.

RESULTS AND DISCUSSION

The results of the hydrogenation of a number of unsaturated hydrocarbons are summarized in Table 1. The precision of the method generally was found to be satisfactory (cf. the three runs with cyclohexene). It should be possible to determine the equiv. weight with an accuracy of about 2 % or better using 5—10 mg of the hydrocarbon. It will present no difficulties to distinguish mono-, di- and polyunsaturated compounds of similar molecular weights or to differentiate, e.g., alkenes with adjacent carbon numbers. The quantitative hydrogenation method should be of special service in the last case, since there is a lack of suitable methods for tracing unusually low-boiling unsaturated hydrocarbons. It has been shown, for example, that such compounds, on carbon number separation, fall into the wrong (next lower) carbon number class which might lead to confusion. An example of such a compound is 3,3-dimethyl-1-butene, which, on carbon number separation, is detached together with the C_5 hydrocarbons [2]. It is uncertain if the method is accurate enough to answer the question whether an unsaturated hydrocarbon, e.g. a C_6 olefin, is straight chain or cyclic, since the equiv. weights in this range do not differ by more

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* We have not found it necessary to make any correction for the vapour pressure of the solvent (about 30 mm at 20°C). The long and narrow tube connecting the hydrogenation flask and the burette probably prevents the solvent vapour from entering the latter space. Moreover, during a considerable part of the hydrogenation period the lower part of the connection tube is nearly sealed by the sample capillary. However, if preferred the hydrogen may be saturated by solvent vapour in the usual way. In that case the vapour pressure of the solvent must, of course, be considered.

Table 1. Quantitative hydrogenation of unsaturated hydrocarbons.

No.	Compound	B.p. °C	Mg	Ml hydrogen			% Error	Equiv. weight	
				Found	Calc.	Diff.		Found	Calc.
1	Cyclohexene	83.0	7.95	2.38	2.38	0.00	0	82.1	82.1
			8.15	2.41	2.43	−0.02	0.8	82.8	82.1
			7.75	2.30	2.30	0.00	0	82.1	82.1
2	*cis*-2-Pentene	36.9	10.40	3.12	3.61	−0.49	13.6	81.1	70.1
3	*trans*-2-Pentene	36.4	5.15	1.78	1.80	−0.02	1.1	70.9	70.1
4	*cis*-2-Octene	125.6	4.60	0.99	1.00	−0.01	1.0	113.3	112.2
5	*trans*-2-Octene	125.0	5.98	1.26	1.26	0.00	0	112.2	112.2
6	3,3-Dimethyl-1-butene	41.2	5.20	1.50	1.50	0.00	0	84.2	84.2
7	2,3,3-Trimethyl-3-butene	77.9	3.95	0.96	0.99	−0.03	3.0	101.3	98·2
8	2-Methyl-2-butene	38.6	7.35	2.53	2.54	−0.01	0.4	70.4	70.1
9	2,3-Dimethyl-2-butene	73.2	10.00	0.40	2.92	−2.52	86.3	614.7	84.2
10	1,2-Hexadiene	76	5.30	3.10	3.10	0.00	0	41.1	41.1
11	1,2-Heptadiene	105	8.76	4.40	4.49	−0.09	2.0	49.1	48.1
12	1,4-Cyclohexadiene	88.5	3.17	1.97	1.97	0.00	0	40.1	40.1
13	1-Hexyne	71.3	7.39	4.20	4.32	−0.12	2.8	42.3	41.1
14	Benzene	80.1	8.80	0.80	8.07	−7.27	90.1	262.3	26.0

than 2—3 %. However, this problem may be solved by gas chromatography using suitable stationary phases (*cf.* Ref. [3]).

As shown by the values in Table 1 there are certain hydrocarbons which consumed far less than the expected amount of hydrogen. Thus, benzene (No. 14) absorbed about one tenth of the theoretical amount of hydrogen in the time generally sufficient to saturate unsaturated hydrocarbons and 2,3-dimethyl-2-butene (No. 9) consumed not much more. That benzene should be quantitatively hydrogenated under the present conditions was hardly to be expected because of its less olefinic nature than the other hydrocarbons in Table 1. 2,3-Dimethyl-2-butene represents the type $R_2C=CR_2$. Since it contains four methyl groups at the carbon-carbon double bond, its approach to the surface of the catalyst might be assumed to be somewhat hindered. Obviously, low values can be expected when hydrogenating this type of alkene using the present method. It will, however, be emphasized that although no quantitative values were obtained, the slow hydrogen consumption indicated that the hydrocarbon was of a type less prone to undergo hydrogenation (*cf.* Fig. 2). The presence of three methyl groups at the carbon-carbon double bond does not hinder the quantitative hydrogenation as seen from the results with 2-methyl-2-butene (No. 8).
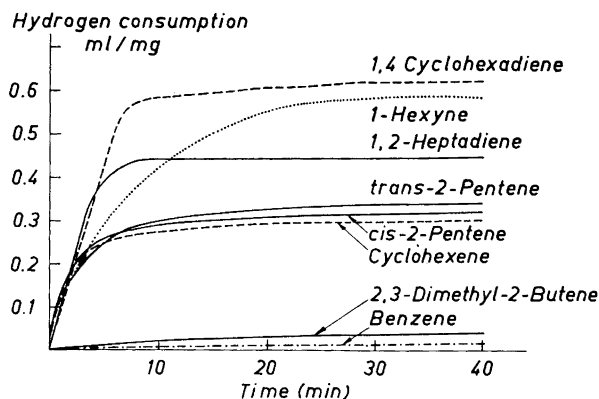
Fig. 2. Hydrogenation curves.

For some yet unknown reason we have not been able to get an accurate value of the hydrogen consumption for *cis*-2-pentene. In repeated runs invariably 10—15 % too low values were obtained. Since *cis*-2-octene was hydrogenated quantitatively without difficulty, the *cis*-2-alkene structure as such seems not to be responsible for the shortcomings. This is also indicated by the "normal" form of the hydrogenation curve (*cf.* Fig. 2). It is most likely that some impurity is present in the original 2-pentene and eluted together with *cis*-2-pentene from the chromatographic column. It may also be that the impurity originates from the stationary phase.

In Fig. 2 the hydrogenation curves of some hydrocarbons are given. It is seen that, for compounds that consume hydrogen quantitatively, the main part of the hydrogenation was completed in 8—10 min. An exception was provided by 1-hexyne in which case the main part of the hydrogenation took a considerable longer time. This result is in agreement with our previous experiences using a qualitative hydrogenation method (*cf.* Ref. [1]). If this difference in hydrogenation velocity is a general phenomenon, it might be possible to distinguish alkynes from alkadienes on the basis of their hydrogenation curves. The low and slow consumption of hydrogen by benzene and 2,3-dimethyl-2-butene is clearly demonstrated by their hydrogenation curves in Fig. 2.

The present investigation has shown that, at 20°C, some unsaturated hydrocarbons could not be hydrogenated quantitatively. This structural dependance of the hydrogenation temperature gives a clue to the structure of the hydrocarbon. It is our intention to investigate this phenomenon further, using lower as well as higher hydrogenation temperatures, in order to study in more detail the relation between structure and hydrogenation temperature for unsaturated hydrocarbons.

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