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# HEATS OF HYDROGENATION IN SOLUTION

## I—A calorimeter for semimicro determinations

*The construction of a calorimeter for measuring heats of catalytic hydrogenation in solution is described. The results obtained for the heats of hydrogenation of some unsaturated hydrocarbons are compared with existing hydrogenation data. Some new improvements are suggested.*

## 1 — INTRODUCTION

Recently, it has been enhanced (1, 2) the importance of the measurement of hydrogenation enthalpies concerning organic molecules. Indeed, it is of great theoretical interest to estimate quantitatively the relative stabilities of the molecules. The hydrogenation method enables the evaluation (3) of effects of steric interaction and conclusions on conformational analysis, can be drawn (4). The prediction of the total energy of the molecule using *ab initio* molecular orbital, calculations requires (5) that the energies of bond separation products are known experimentally if not theoretically in the case of a large number of organic molecules to which the process of complete hydrogenation is separated into two steps: bond separation reaction and complete hydrogenation reaction. Effects of configuration or strain (6) in sets of molecules of the same type, as well as, resonance energies (7), can be also evaluated from the thermochemical data. Many of these conclusions can be further tested by spectroscopic methods and related with spectroscopic data.

The important reasons mentioned above and the fact that in many cases it is of the most interest to determine thermochemical data from very small amounts of organic compounds led us to construct a calorimeter that could afford reproducible and accurate results in such cases. The device is of a previous design (2) with some modifications we found to be necessary in order it could be operative.

## 2 — EXPERIMENTAL

### 2.1 — APPARATUS

The calorimeter consists of a reaction vessel immersed in a water bath within a cylindrical glass tub as shown in fig. 1a. The reaction vessel is a cylindrical glass flask of about 120 c.c. capacity whose top is tightly closed with a rubber stopper. Through the rubber stopper are fixed two glass tubes and a hypodermic needle. The longer glass tube (5 mm diameter) holds the thermistor which is immersed in paraffin oil (low heat capacity) the shorter tube (10 mm diameter) is the guide tube for sample insertion and its bottom has been adapted with

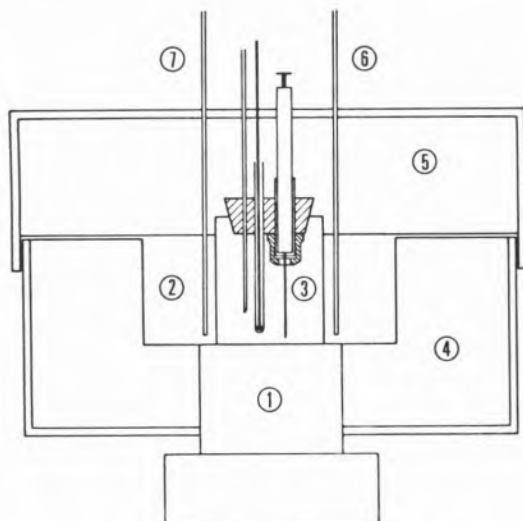


Fig. 1a — Schematic diagram of apparatus assembly:  
1 — Magnetic stirrer; 2 — Water bath;  
3 — Reaction vessel; 4 — Insulating box;  
5 — Lid of the insulating box; 6-7 — Thermometers

a rubber cap having a hole in the middle. A gasliq cromatography insertion sample rubber is well adjusted over the hole inside the cap as shown in fig. 1b. The admittance of known quantities of samples is made by means of a hypodermic micro-syringe which descends until the level of the rubber cap. By this way the sample is admitted very close to the liquid phase and so the flying about or splashing off on the walls is avoided. The fixed hypodermic needle constitutes the hydrogen inlet and its top is connected through a Luer joint to the hydrogen line. The connection Luer joint and tubing had to be cemented with a special glue (Dow Corning) so that any leak could be avoided.

A metallic frame was placed on the top of the reaction vessel holding simultaneously the rubber stopper and the rim of the reaction vessel to prevent the going out of the rubber stopper when the pressure inside the reaction vessel is about two atmosferes.

In the water bath surrounding the reaction vessel there are a glass rod stirrer and two thermometers, one of them is a Beckmann Thermometer previously calibrated. The cylindrical glass tub has 14 cm diameter. The temperature of the water bath can be controled at  $20 \pm 0.01^\circ\text{C}$ .

The whole system, reaction vessel and water bath, is enclosed in an insulating box with very thick walls of about 6 cm (fig. 1a). The middle of the bottom of the box is opened so that a magnetic stirrer

can be fitted. To this box is adjusted a lid with about the same height as the box and the same thickness of the walls. Through the lid three holes were made in the direction of the reaction vessel and three holes were made in the direction of the water bath in such a way that the whole system was completely insulated once they were fulfilled with the corresponding solids parts (glass rod stirrer, thermometer, hydrogen line tubing, thermistor wires, microsyringe or a corresponding insulating material). The insulating material used was sferovite, being the whole external surface covered with hydraulic prensed pasteboard. This box was in a temperature controlled room ( $20 \pm 1^\circ\text{C}$ ).

Temperature changes in the reaction vessel were detected by means of a thermistor.

We used a thermistor as the unknown arm of a Wheatstone bridge (Lionmount Type BW6) and temperature changes translated into resistance

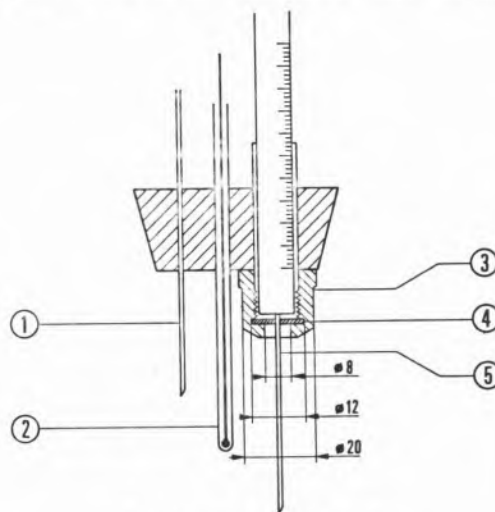


Fig. 1b — Detail of fig. 1a:  
1 — Hypodermic needle; 2 — Thermistor; 3 — Rubber cap;  
4 — Insertion sample rubber; 5 — Microsyringe needle

changes were read by the deflection of a lightspot galvanometer (Kipp Type AL3). A transistat was used as a power unit D.C. and the potential across the bridge was about 6 Volt kept constant within  $\pm 0.05\text{ V}$ . The Wheatstone bridge has an accuracy of  $\pm 0.1\%$ . The hydrogen line is represented schematically in fig. 2. We used a Hopkins Head to prevent the coming out of vapours of glacial acetic acid to the hydrogen line during the evacuation of the system by a rotary pump.

## 2.2 — REAGENTS

- Solvent: Glacial acetic acid (RPE).
- Catalyst: palladium on activated carbon 5 % Pd (Fluka AG, Buchs SG).

Samples to be hydrogenated:

- 1-Hexene (Schuchardt München);
- 1-Octene (Schuchardt München);
- Cyclohexene (Schuchardt München);
- d-Limonene (Schuchardt München);
- 2,3-dimethyl-2-pentene (K & K Laboratories Inc.);
- Myrcene (K & K Laboratories Inc.).

The purity of the samples was tested by gas liquid chromatography and by mass spectrometry.

## 2.3 — PROCEDURE

The electrical Wheatstone bridge circuitry is switched on immediately after solvent (50 ml) and catalyst (0.5 g) are introduced in the reaction vessel which is then placed in the water bath and the whole system is closed adjusting the lid to the insulating box. Reaction vessel and hydrogen line are evacuated until a pressure of a few mm Hg is reached. The pressure is measured with a manometer of mercury with one of the arms opened to the atmosphere (see Fig. 2). Current is then allowed to pass through the Wheatstone bridge which is balanced to zero galvanometer deflection. The magnetic stirrer circuitry is switched on and to avoid fluctuation due to the mains a stabilizer has been introduced so that a uniform rate of stirring was produced. Hydrogen goes into the reaction vessel until a pressure of about 2 atmosferes is reached. Then the reaction vessel is flushed several times with hydrogen and finally filled to a pressure of two atmosferes which is kept constant during the experiment. After a few minutes, Wheatstone bridge has to be balanced again because heat of reduction is developped due to reduction of the catalyst. At this point readings every 30 seconds of galvanometer deflections are recorded and a base line can be established. A microvolume of sample less than 50  $\mu$ l is then inserted by the

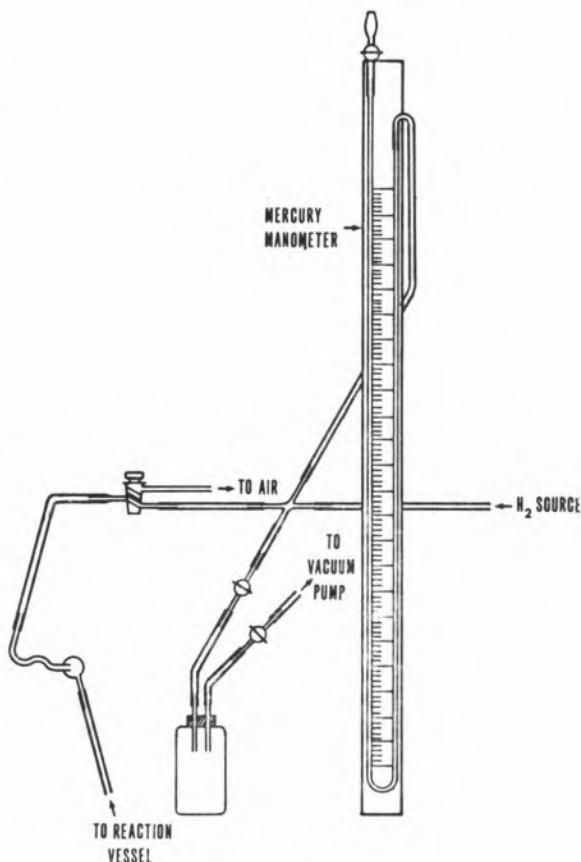


Fig. 2

hypodermic syringe (100  $\mu$ l volume type Hamilton) and the galvanometer readings every 30 seconds continue being recorded even after reaction is over. Time of reaction is very short less than one minute. The whole time for one experiment is around ten, twelve minutes from the beginning of the establishment of the base line. A second experiment with a same sample is run after initial thermal conditions are re-established. This can be done changing equal volumes of cooled water with warmed water, after having stopped the stirrer. In this way six or seven experiments can be carried out having good reproducibility. Independent experiments were also done so that complete hydrogenation could be tested. Bromine water with a known calculated concentration was added to the solution once the experiment was over. About twenty experiments were made for most of the compounds including three independent experiments for each one. The calibration of the apparatus was done using 1-hexene as a calorimetric standard. About thirty

five experiments including five independent experiments were effectuated. Considering the proportionality between galvanometer deflection per millimole and heat evolved during reaction, heat of hydrogenation can be determined (2) assuming the value of 30.3 kcal/mole for the heat of hydrogenation of 1-hexene.

To obtain final results for heats of hydrogenation,  $\Delta H$ , the value of galvanometer deflection corresponding to the variation of temperature due to the heat evolved during the hydrogenation reaction is obtained by a graphical method (8).

We made the extrapolation of the linear equation corresponding to the initial and final periods. The straight lines were obtained by least squares method.

### 3 — RESULTS AND DISCUSSION

The final computed results of these experiments are average values and are given in the table I together with the corresponding average deviation from the mean. None of these results is corrected for heat of solution so in the following discussion this has to be accounted for.

Comparing the results obtained with previous work we can see a good agreement. The value obtained for 2,3-dimethyl-2-pentene looks fairly reasonable when compared with values obtained (3) for 2,4-dimethyl-1-pentene and 2,4-dimethyl-2-pentene. Monoterpene compounds show somehow low values which might be due to structure effects.

Table I

*Heat of hydrogenation of some unsaturated hydrocarbons*

Compound	$\Delta H$ (kcal/mole)	$\Delta H_{lit}$ (kcal/mole)
Cyclohexene	$-28.7 \pm 1.2$	$-28.6(a)$ ; $-27.1(b)$
1-octene	$-31.1 \pm 1.4$	$-30.1(c)$
2,3-dimethyl-2-pentene	$-27.0 \pm 1.1$	
Limonene	$-51.4 \pm 2.3$	$-54(d)$
Myrcene	$-64.4 \pm 3.1$	

(a) Reference (9); (b) reference (10); (c) reference (1); (d) reference (11).

To test the validity of these conclusions some more experiments on different monoterpene compounds are planned. To increase the accuracy of experimental results we intend to prosecute our experiments with a Wheatstone bridge of  $\pm 0.001\%$  accuracy. A further development consists to employ two thermistors in series, a passive and the other one as active. The unknown arm of the Wheatstone bridge corresponds to the active one. We mean as passive the thermistor is within an identical reaction vessel but there is no reaction in.

### ACKNOWLEDGMENTS

One of us (M. T. R. L.) thanks the Instituto de Alta Cultura for a research grant.

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Received 11. June. 1974.

### RESUMO

Descreve-se a construção de um calorímetro para medição de calores de hidrogenação catalítica, em solução. Comparam-se os resultados obtidos para os valores de calores de hidrogenação de alguns hidrocarbonetos insaturados com dados existentes. Sugerem-se alguns melhoramentos.