

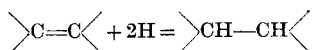
CHAPTER I

OLEFINES

SOLID AND LIQUID OLEFINES

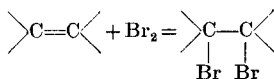
The characteristic property of olefines, their combining directly with certain atoms or groups, is used for the estimation of unsaturated compounds. The reagents and the experimental conditions must be controlled carefully to make the addition quantitative and to prevent side reactions occurring. The rate of addition varies considerably with the types of grouping attached to the olefinic linkage and also with the degree of substitution. The following reactions have been used to measure the degree of unsaturation.

Hydrogenation:



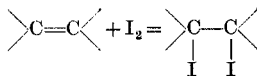
- A. Macro-hydrogenation.
- B. Micro-hydrogenation.

Bromine number:



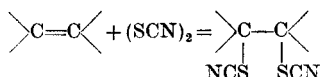
- A. Direct titration.
- B. Electrometric titration.
- C. Bromine absorption.

Iodine number:



- A. Wijs' method.
- B. Hanus' method.
- C. Rosenmund-Kuhnhenh's method.

Thiocyanogen number:



Cambridge University Press

978-0-521-11275-8 - Estimation of Organic Compounds

F. Wild

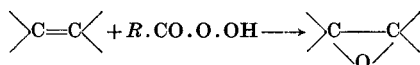
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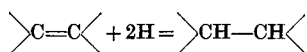
OLEFINES

Estimation by peracids:



Miscellaneous:

HYDROGENATION



Catalytic hydrogenation is used extensively to determine the degree of unsaturation in organic compounds by measuring the volume of hydrogen absorbed by a weighed amount of the substance. The method is accurate, and if necessary it can be done on a micro-scale. The experimental conditions, such as temperature, hydrogenation pressure, catalyst, solvent and purity of the compound, are all interdependent, so that it is impossible to give precise details for the reduction of a particular type of structure. Olefines normally are saturated under mild conditions, and it is convenient to carry out the reaction at atmospheric pressure.

The apparatus is a hydrogen reservoir connected to a reaction vessel which can be shaken mechanically and heated if necessary. The system is filled with hydrogen, equilibrium is reached between the catalyst and hydrogen, a weighed amount of the substance is introduced into the reaction vessel, and the hydrogen absorbed on shaking, is measured either by a reduction in the volume or by a fall in the pressure. Numerous forms of apparatus have been described by which these changes can be followed in the laboratory.¹

The types of micro-apparatus so far constructed have been based on the principle of the Barcroft differential manometer.² Two similar flasks are connected to a hydrogen reservoir and to

¹ See C. Paal and J. Gerum, *Ber.* 1908, **41**, 805-17; R. Willstätter and D. Hatt, *ibid.* 1912, **45**, 71-81; A. Skita and W. A. Meyer, *ibid.* 1912, **45**, 3589-95; O. Stark, *ibid.* 1913, **46**, 2335-6; and for pressures up to 3.5 atm. see R. Adams and V. Voorhees, *Org. Syn.* **8**, 10-16, col. vol. 1st ed. pp. 53-9, 2nd ed. pp. 61-7; for pressures up to 300 atm. and temperatures up to 400° C. see H. Adkins, *J. Amer. Chem. Soc.* 1933, **55**, 4272-9; for pressures up to 300 atm. and temperatures up to 250° C. see A. R. Gilson and T. W. Baskerville, *Chem. and Ind.* 1943, **62**, 450-2 (fig. 1).

² J. Barcroft, *J. Physiol.* 1908, **37**, 212.

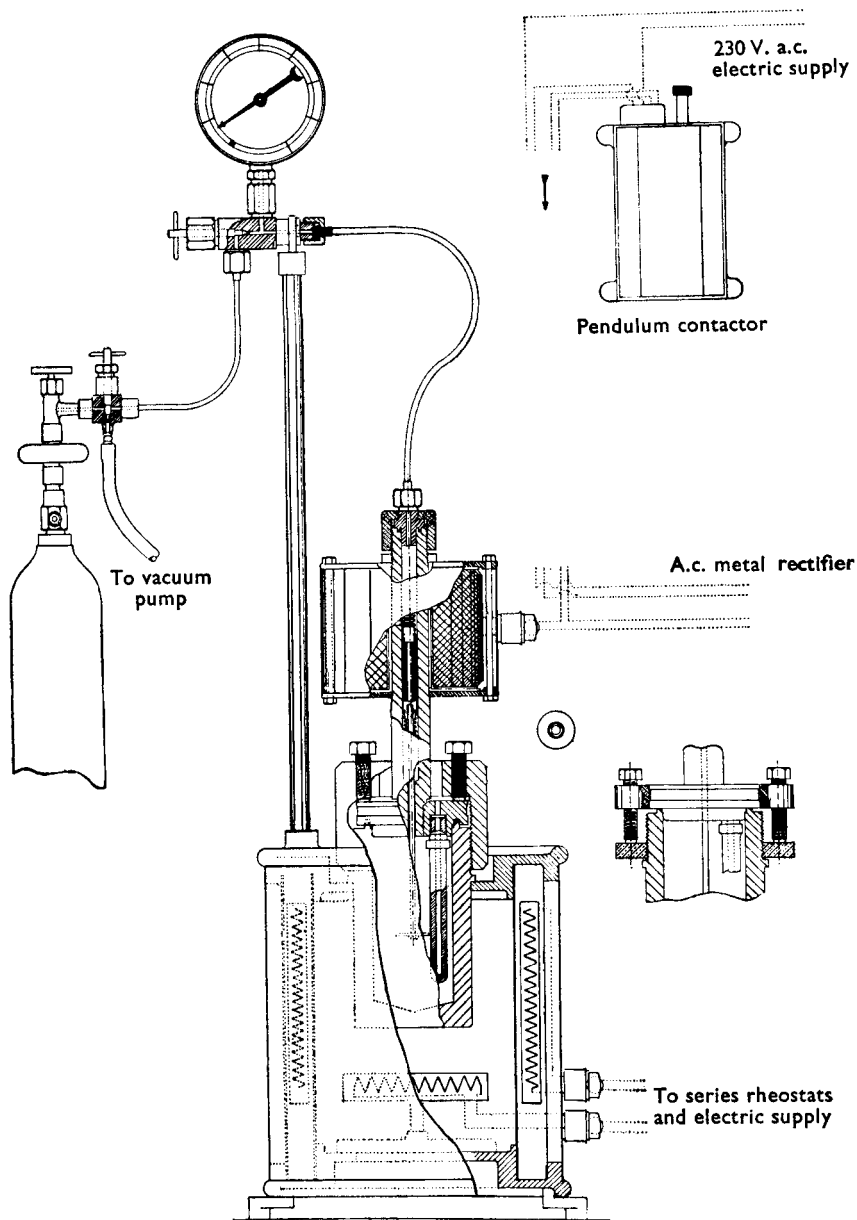


Fig. 1.

each other through a sensitive capillary tube filled with dibutyl phthalate or clove oil. In most forms of the apparatus the hydrogenation is done in one flask and solvent is added to the other which is used as a compensating vessel,¹ although sometimes it is used for the reduction of a control substance and the final difference in the volume of hydrogen absorbed is measured.² The latter method is used frequently but requires very rigid thermostatic control for accurate results. It has been used to compensate empirically for the incomplete reduction of substances, such as the polyenes.³ In all micro-hydrogenations it is essential that each piece of apparatus should be perfectly clean and all chemicals pure, as traces of impurity frequently cause inconsistent results.⁴

A wide variety of catalysts, including platinum, palladium, nickel, copper chromite and a number of oxides, have been described. Platinum and palladium in the colloidal and amorphous forms, and less often Raney nickel, are used most frequently for the quantitative reduction of double bonds. A very active platinum catalyst (Adams' catalyst) is prepared by reducing the hydrated platinum oxide ($\text{PtO}_2 \cdot \text{H}_2\text{O}$) by shaking with hydrogen at room temperature. The dioxide is formed by fusion of chloroplatinic acid with sodium, or potassium, nitrite at $500\text{--}550^\circ \text{C}$.⁵ The chloroplatinic acid is recovered by dissolving the residue in aqua regia, but if the catalyst has been poisoned extensively it should be purified by making ammonium chloroplatinate and using this as the starting material for the fusion.⁶ The fusion can be carried out successfully in a beaker, but some skill is needed to produce a very

¹ J. H. C. Smith, *J. Biol. Chem.* 1932, **96**, 35–51; H. Jackson and R. N. Jones, *J. Chem. Soc.* 1936, pp. 895–9; H. Jackson, *J. Soc. Chem. Ind.* 1938, **57**, 1076–7; J. F. Hyde and H. W. Scherp, *J. Amer. Chem. Soc.* 1930, **52**, 3359–63.

² R. Kuhn and E. E. Möller, *Angew. Chem.* 1934, **47**, 145–9.

³ Cf. R. F. Milton and W. A. Waters, *Methods of Quantitative Microanalysis*, pp. 568–9.

⁴ A. E. Gillam and M. S. El Ridi, *Biochem. J.* 1936, **30**, 1735–42.

⁵ R. Adams, V. Voorhees and R. L. Shriner, *Org. Syn.* **8**, 92–9, col. vol. 1st ed. pp. 452–60, 2nd ed. pp. 463–70; A. H. Cook and R. P. Linstead, *J. Chem. Soc.* 1934, pp. 946–56.

⁶ E. L. Baldesweiler and L. A. Mikeska, *J. Amer. Chem. Soc.* 1935, **57**, 977–83; W. F. Bruce, *ibid.* 1936, **58**, 687–8 and *Org. Syn.* **17**, 98.

active catalyst. A fusion apparatus has been described by Short.¹ Platinum black can be used either in the amorphous form or supported on an inert carrier. The former is prepared by reducing chloroplatinic acid with formaldehyde in the presence of sodium hydroxide,² and the latter by warming a suspension of the inert material in chloroplatinic acid, precipitating platinum hydroxide on the carrier and reducing. The carriers used most frequently are barium sulphate, charcoal, calcium carbonate, kieselguhr and silica gel.³ Palladium catalysts are prepared by methods similar to those used for platinum. Soluble salts can be reduced with formaldehyde in the presence of sodium hydroxide;⁴ the oxide, prepared by fusion of the chloride with sodium nitrite, can be reduced with hydrogen at room temperature;⁵ and palladium black can be deposited on an inert carrier as, for instance, barium sulphate,⁶ activated charcoal,⁷ calcium or strontium carbonate,⁸ silica gel⁹ or kieselguhr.¹⁰ Until recently the nickel catalyst most commonly used in the laboratory was prepared by impregnating a porous support with a nickel salt, forming the oxide and finally reducing with hydrogen at 300–400° C. This form of the catalyst could not be used at atmospheric pressure and room temperature, and it was not possible to use nickel under these conditions until 1927 when

¹ W. F. Short, *J. Soc. Chem. Ind.* 1936, **55**, 14T.¹

² R. Feulgen, *Ber.* 1921, **54**, 560–1; O. Loew, *ibid.* 1890, **23**, 289–90; R. Willstätter and D. Hatt, *loc. cit.* (p. 2, n. 1); R. Willstätter and O. Waldschmidt-Leitz, *ibid.* 1921, **54**, 113–38.

³ Houben-Weyl, *Die Methoden der organischen Chemie*, **2**, 499; H. Kaffer, *Ber.* 1924, **57**, 1261–5; N. D. Zelinsky and M. B. Turowa-Pollak, *ibid.* 1925, **58**, 1298–1303; M. Latshaw and L. H. Reyerson, *J. Amer. Chem. Soc.* 1925, **47**, 610–12; V. N. Morris and L. H. Reyerson, *J. Phys. Chem.* 1927, **31**, 1220–9; *ibid.* 1927, **31**, 1332–7.

⁴ Houben-Weyl, *Die Methoden der organischen Chemie*, **2**, 498.

⁵ R. L. Shriner and R. Adams, *J. Amer. Chem. Soc.* 1924, **46**, 1683; cf. R. Adams, V. Voorhees and R. L. Shriner, *loc. cit.* (p. 4, n. 5); A. H. Cook and R. P. Linstead, *loc. cit.* (p. 4, n. 5); W. F. Bruce, *loc. cit.* (p. 4, n. 6).

⁶ E. Schmidt, *Ber.* 1919, **52**, 400–13; R. L. Shriner and R. Adams, *loc. cit.* (p. 5, n. 5).

⁷ W. H. Hartung, *J. Amer. Chem. Soc.* 1928, **50**, 3370–4; E. Ott and R. Schröter, *Ber.* 1927, **60**, 786–804; F. Mayer and G. Stamm, *ibid.* 1923, **56**, 1424–33; C. Mannich and E. Thiele, *Ber. deut. pharm. Ges.* 1916, **26**, 36–48; *J. Soc. Chem. Ind.* 1916, **35**, 548–9.

⁸ M. Busch and H. Stöve, *Ber.* 1916, **49**, 1063–71.

⁹ M. Latshaw and L. H. Reyerson, *loc. cit.* (p. 5, n. 3).

¹⁰ Th. Sabalitschka and W. Moses, *Ber.* 1927, **60**, 800–1.

Raney prepared a catalyst of greatly increased activity. An improved method of preparation has been described recently which gives a highly active catalyst ('W-6') which can be used for hydrogenation at low pressures.¹ A nickel-aluminium alloy, corresponding to NiAl_2 , is prepared and the aluminium is dissolved out with sodium hydroxide.² The residual nickel is pyrophoric and is kept under water or under a suitable organic liquid. The amount of this catalyst required for a given hydrogenation is many times greater than for a catalyst of nickel on kieselguhr.

The activity of catalysts frequently shows a marked response to the presence of traces of promoters, and, indeed, the most successful catalysts are often very impure. Adams' catalyst contains sodium salts and Raney nickel contains aluminium and usually cobalt, and part of their activity probably arises from these impurities. An increase in activity may be gained by adding promoters. The activity of Raney nickel is increased greatly by the addition of small amounts of metals such as platinum, copper, zinc, chromium, molybdenum, iron and caesium;³ small amounts of mineral acids increase the rate of hydrogenation of benzene using platinum black,⁴ and benzoyl peroxide frequently increases the velocity of hydrogenation.⁵ The efficiency of the catalysts can be reduced partially or completely by poisons. The former is sometimes done deliberately to stop the reduction at an intermediate stage, as in the hydrogenation of an acid chloride to an aldehyde,⁶ but the latter arises from impurities or from the reaction. Mercury is described as a poison, although small quantities of the metal can be added to the reaction vessel and seem to have little effect when palladium

¹ H. R. Billica and H. Adkins, *Org. Syn.* **29**, 24-9.

² M. Raney, U.S. pat. 1,628,190; H. Adkins and H. R. Billica, *J. Amer. Chem. Soc.* **1948**, **70**, 695-8; L. W. Covert and H. Adkins, *ibid.* **1932**, **54**, 4116-17; R. Mazingo, *Org. Syn.* **21**, 15-17.

³ J. R. Reasenberg, E. Lieber and G. B. L. Smith, *J. Amer. Chem. Soc.* **1939**, **61**, 384-7; M. Delépine and A. Horeau, *Compt. rend.* **1935**, **200**, 1414.

⁴ K. Kindler, E. Brandt and E. Gehlhaar, *Ann.* **1924**, **511**, 209-12; K. Kindler and W. Peschke, *ibid.* **1935**, **519**, 291-6; J. H. Brown, H. W. Durand and C. S. Marvel, *J. Amer. Chem. Soc.* **1936**, **58**, 1594-6.

⁵ G. Thomson, *ibid.* **1934**, **56**, 2744-7.

⁶ K. W. Rosenmund and F. Zetzsche, *Ber.* **1921**, **54**, 425-40; K. W. Rosenmund, F. Zetzsche and G. Weiler, *ibid.* **1923**, **56**, 1481-7.

charcoal is the catalyst.¹ Unsaturated compounds prepared by dehydration with thionyl chloride usually resist hydrogenation, as they still retain traces of sulphur products. These can be removed generally by shaking with aluminium amalgam in moist ether.² Other sulphur compounds, including vulcanized rubber, have been described as poisons, and it is recommended that any rubber used in a hydrogenation apparatus should be freed from sulphur as far as possible by boiling with sodium hydroxide and water.³ It has been suggested that the poisoning elements, such as sulphur, selenium, tellurium, phosphorus and arsenic, are ineffective as poisons when they have a complete octet of electrons.⁴ Another form of poisoning is caused by the failure of the catalyst to desorb a product quickly. A high pressure of hydrogen often minimizes this effect by tending to increase the area of the catalyst covered with hydrogen. In the same way high pressures reduce the effect of small amounts of poisons in the reaction mixture.

The catalyst is dispersed in the solvent and is brought into close contact with the organic material and hydrogen either by shaking or stirring. Solvents which are commonly used are ethyl alcohol, acetic acid, ethyl acetate, ether, dioxane, and saturated hydrocarbons such as *n*-hexane, decalin, *cyclohexane* and methyl-*cyclohexane*. Attempts to correlate the rate of hydrogenation with the nature of the solvent have been unsuccessful so far, although it has been shown that the product sometimes depends on the solvent. The hydrogenation of triphenylmethane in ethyl alcohol stops when two of the three aromatic nuclei have been reduced, but all three rings are saturated when methyl-*cyclohexane* is the solvent.⁵

The rate of hydrogenation and the nature of the final product can be varied by changes in the experimental conditions, although the latter is rare with olefines, as normally they reduce

¹ C. Paal and W. Hartmann, *Ber.* 1918, **51**, 711–37.

² P. Gaubert, R. P. Linstead and H. N. Rydon, *J. Chem. Soc.* 1937, pp. 1974–9.

³ R. Adams and V. Voorhees, *loc. cit.* (p. 2, n. 1); cf. R. Truffault, *Bull. Soc. Chim.* 1935, [v], **2**, 244–53.

⁴ E. B. Maxted and R. W. D. Morris, *J. Chem. Soc.* 1937, pp. 252–6.

⁵ H. Adkins, W. H. Zartman and H. Cramer, *J. Amer. Chem. Soc.* 1931, **53**, 1425–8.

under very mild conditions. Heating the reaction mixture usually increases the rate of hydrogenation, but the effect may be less than anticipated as the partial pressure of the hydrogen is reduced by a rise in the vapour pressure of the solvent. This is one way in which the solvent can affect the reaction indirectly. An increase in pressure also increases the rate of reduction, but the effect varies greatly with the particular catalyst used and is most marked with nickel. The rate of absorption of hydrogen depends upon the surface area of the catalyst, so that the amount of solid present and its state of division are important. Complete reduction of many polyenes, such as the carotenoids, is impossible unless a relatively large amount of the catalyst is used (e.g. 0.5–2.5 g. of platinum per g. of compound). The hydrogen, the organic compound and the catalyst are brought into contact by shaking, and the rate of absorption can be affected considerably by changes in the rate of shaking.

The selectivity in action of catalysts must also be considered. Nickel is more active toward olefinic linkages than most of the oxide catalysts. The esters of unsaturated acids can be hydrogenated to unsaturated alcohols with zinc chromite at 250° C., whereas the double bond only is reduced with nickel below this temperature. The catalysts become less selective as the temperature is raised, and there is an increased probability of forming the saturated hydrocarbon.

The olefinic linkage is one of the groups reduced most readily and any of the common catalysts can be used. The simple alkenes react with hydrogen and a catalyst at room temperature and atmospheric pressure, but reduction becomes more difficult as the degree of substitution increases at the double bond.¹ A completely substituted ethylene, such as dodecahydrophenanthrene where the double bond is common to two ring systems, may be very resistant to hydrogenation.² Conjugation does not always retard hydrogenation, but there are many examples recorded where more drastic conditions are needed. When a double bond is conjugated to a carbonyl or carboxyl group it is

¹ W. H. Zartman and H. Adkins, *J. Amer. Chem. Soc.* 1932, **54**, 1668–74; S. V. Lebedev and M. Platonov, *J. Chem. Soc.* 1930, pp. 321–36.

² J. R. Durland and H. Adkins, *J. Amer. Chem. Soc.* 1938, **60**, 1501–5.

hydrogenated more slowly than an isolated double bond (e.g. the $\gamma\delta$ double bond in sorbic acid is easier to reduce than the $\alpha\beta$ bond which is in conjugation).¹ The selective reduction of a double bond in a side chain to an aromatic ring is often possible owing to the ease with which the olefinic linkage is hydrogenated preferentially. The *cis* form of an ethylenic compound usually hydrogenates more quickly than the *trans*.²

The breaking of a bond which can take place during hydrogenation is usually called hydrogenolysis. The conditions generally are drastic, and normally hydrogenolysis can be ignored for hydrogenations at room temperature and atmospheric pressure. A halogen group, however, can be replaced under these conditions in many aliphatic compounds, and even the relatively inert aromatic halogen compounds can be dehalogenated and hydrogenated to the *cycloparaffins* with Adams' catalyst at 3 atm. pressure and a temperature of 50–70° C. This must be taken into account when unsaturated halides are estimated quantitatively by hydrogenation.

A. Macro-hydrogenation

A hydrogenation apparatus is as shown in fig. 2.

The taps and ground-glass joints of the apparatus should be examined carefully before the experiments to ensure that they are greased properly and free from striations. Vacuum grease only must be used.

The reaction flask *F* containing the catalyst and some of the liquid which is used as the solvent for the olefine (20–50 ml.) is attached to the apparatus and held firmly in position by suitable clips (rubber bands stretched between metal holders are satisfactory). The burettes *B*₁ (500 ml.) and *B*₂ (250 ml.) are filled with water and, with the taps *T*₁ and *T*₅ open and *T*₂, *T*₃ and *T*₄ closed, the apparatus is evacuated by a vacuum, or a good water pump connected to *T*₁ through a trap. The liquid in *F* is degassed by shaking the flask whilst the air is being sucked out of the

¹ E. H. Farmer and R. A. E. Galley, *J. Chem. Soc.* 1933, pp. 687–96.

² C. Paal and H. Schiedewitz, *Ber.* 1927, **60**, 1221–8; 1930, **63**, 766–78; cf. C. Weygand, A. Werner and W. Lazendorf, *J. prakt. Chem.* 1938, **151** [ii], 231–2.

apparatus. When the manometer M shows a steady state T_1 is closed and the apparatus filled with hydrogen from a cylinder which is connected to T_2 through a simple mercury valve, V , which is necessary to reduce the pressure to atmospheric. T_2 is

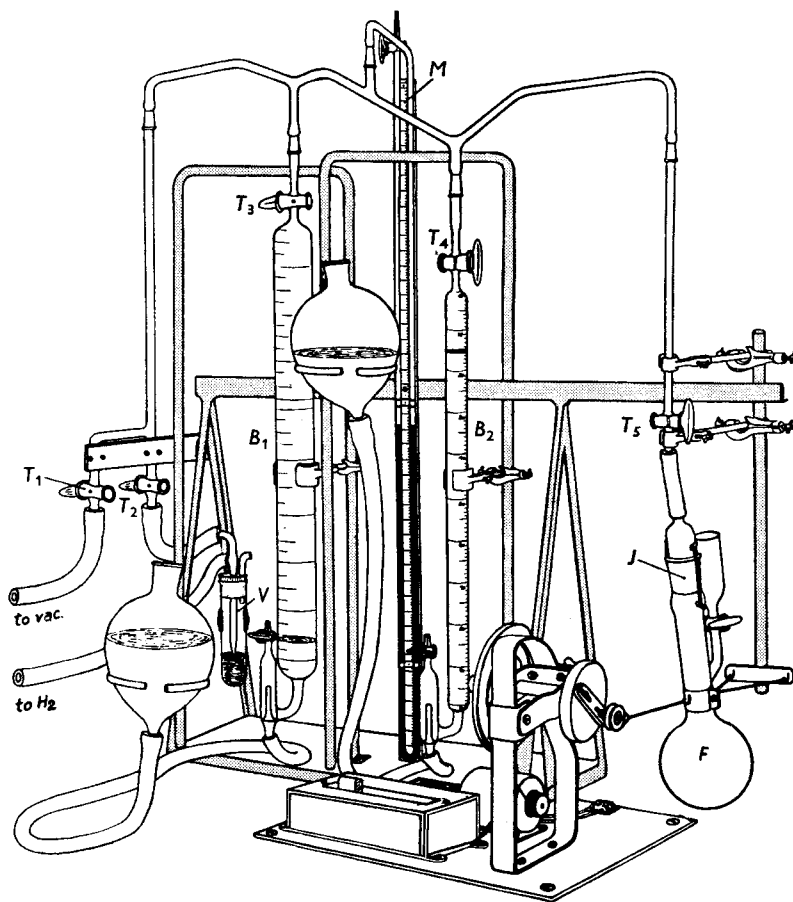


Fig. 2.

closed, T_1 is opened, the apparatus is evacuated again, T_1 and T_5 are closed and the apparatus, including the burettes, is filled with hydrogen. T_5 is opened and T_2 and T_3 are closed. The flask is shaken mechanically until no more hydrogen is absorbed from burette B_2 which corresponds to the complete reduction of the catalyst. A solution of the olefine is added to the reaction flask