TABLE V

CALCULATION OF α-SOLID SOLUTION COMPOSITIONS

(1) Temp., °K.	(2) N_2 (Endo)	(3) a_2	(4) a_2'	(5) N_2'	(6) $N_2' a_2' = a_2$	(7) N_2 (calcd.)	(8) N_2 (exp.)
412	0.440	0.465	0.485	0.959			
420	.485	.508	.513	.960	0.493	0.467	0.47
440	.587	.605	.584	.970	.566	.547	.55
460	.692	.705	.659	.955	.642	.628	.62
480	.755	.765	.736	.980	.721	.710	.70
500	.835	.840	.817	.987	.807	.800	.79
520	.915	.917	.898	.992	.891	.887	.89

from the activity curve and are shown in column (7). These values are in good agreement with Würschmidt's smoothed curve, column (8), which lies above that of Endo.

Summary

1. The activities and relative heat contents of tin and bismuth in their liquid alloys have been determined from electromotive force studies.

2. These thermodynamic data have been compared with published equilibrium data for the system. The β solid solution at the eutectic has been calculated to contain 20% of bismuth, while the α solid solution contains 2.4% of tin. The α liquidus points obtained by Würschmidt are in good agreement with those calculated from these data, while Endo's curve seems to be too low.

Heats of Catalytic Hydrogenation in Solution. I. Apparatus, Technique, and the Heats of Hydrogenation of Certain Pairs of Stereoisomers

BY R. BRANSTON WILLIAMS

For some years past, Kistiakowsky and his co-workers[1] have been engaged in the direct measurement of the heats of certain catalytic reactions in the vapor phase. The application of the new method, however, is limited, being restricted to compounds which are appreciably volatile at the temperature at which the reactions are carried out and so it seemed desirable to attempt to extend the method to the liquid phase, where the same restriction as to the substances suitable for study does not hold.

The reactions studied have been of the type

X (liquid or solid) + H_2 (gas) ⟶ Y (in solution)
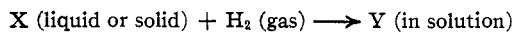
and to obtain values applicable to the completely gaseous reactions

X (gas) + H_2 (gas) ⟶ Y (gas)
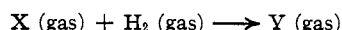
various corrections have to be applied. Thus the relationship between ΔH, the molar heat of a reaction of the type studied, and ΔH_g, the molar heat of the completely gaseous reaction, is given by

$$\Delta H_g = \Delta H - (_xL_v - _yL_v) - L_s \quad (1)$$

when X and Y are both liquids at the temperature of the measurements, and by

$$\Delta H_g = \Delta H - (_xL_v - _yL_v) - (_xL_f - _yL_f) - L_s \quad (2)$$

when X and Y are both solids. $_xL_v$, $_xL_f$, $_yL_v$, and $_yL_f$, are the molar latent heats of vaporization and fusion of X and Y, respectively, and L_s is the molar heat of solution of Y in the solvent used, all the terms being positive when heat is absorbed, and applying at the temperature of the measurements. In the present work, heats of solution have been determined directly, but latent heats have been taken from the literature.

The accuracy of the results yielded by the calorimeter has been tested by measuring the heat of hydrogenation of n-heptene-1, and comparing the result obtained with that yielded for the same substance by the vapor method.

Method

The determinations of heats of hydrogenation and of solution involved in this investigation were carried out in the usual way by measuring the change in temperature of the calorimeter and contents due to the hydrogenation or solution of a known quantity of material, and then determining the electrical equivalent of the calorimeter and contents over the same temperature range.

(1) Kistiakowsky, et al., THIS JOURNAL, **57**, 65 (1935); **57**, 876 (1935); **58**, 137 (1936); **58**, 146 (1936); **59**, 831 (1937); **60**, 440 (1938); **60**, 2764 (1938); **61**, 1868 (1939); Chem. Rev., **20**, 181 (1937).

In the computation of the true temperature change accompanying a hydrogenation, solution, or electrical calibration, the standard calorimetric procedure was followed, the correction to be applied to $\Delta\theta$, the observed temperature change, being calculated from a knowledge of the rate of cooling (or heating) of the calorimeter and contents, due only to heat exchange with the surroundings, at two different temperatures.

Apparatus

The calorimeter consists of two parts, the vessel and the head, and is shown in Fig. 1. The vessel is composed of a spherical dewar flask, of about 500 cc. capacity, with two necks. The larger of these is of 42 mm. diameter, and its end is a male ground-glass joint. The smaller is of 10 mm. diameter, and through it the thermometer is inserted. By means of three small glass legs a hollow glass cylinder, about 4.5 cm. high and about 4 cm. in diameter is fixed to the bottom of the inside of the flask. At one point on the rim, under the large neck, is a small glass spike used for breaking the glass ampoules containing the material to be hydrogenated or dissolved.
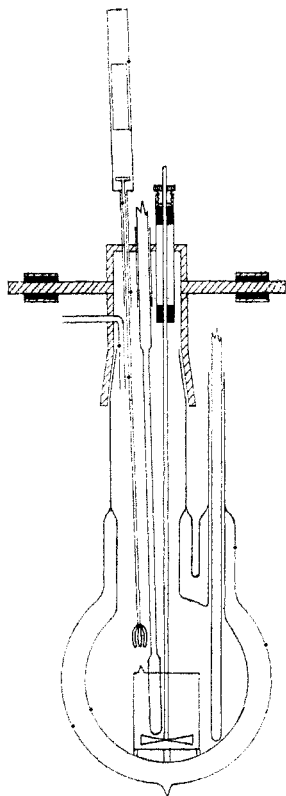

Fig. 1.

The calorimeter head consists of a hollow brass cylinder with the upper end closed. Its lower end forms a female ground joint which fits over the male ground-glass joint at the top of the large neck of the calorimeter vessel, the two parts being held together by means of two phosphor-bronze springs (not shown). The joint is made gastight by means of low-vapor pressure grease. Each of the side arms, also of brass, carries a rubber ring over which a brass ring is lightly fitted. When the calorimeter is in use,

it is supported by holding these brass rings in clamps; the rubber rings then act as bearings, allowing the calorimeter to be shaken regularly by means of an eccentric and a synchronous electric motor. This shaking ensures that the hydrogenation is sufficiently rapid.

Through the top of the head are fixed (1) a guide-tube for the electrical heater, (2) a stainless steel stirrer, and (3) a device for holding and breaking the ampoules containing the material to be hydrogenated or dissolved. This device consists of a thin stainless steel rod, held in a guide-tube soldered through the top of the calorimeter head. To its lower end is attached a three-pronged stainless steel clip, and the position of the guide-tube is so arranged that the somewhat concave bottom of the ampoule, held in the clip, rests on the glass spike on the rim of the hollow glass cylinder fixed to the bottom of the dewar flask. To break the ampoule, a piece of soft iron is raised by means of a solenoid placed around the enclosing brass tube and is then allowed to drop on to the top of the stainless steel rod, the bottom of the ampoule being thus forced against the glass spike, which shatters it.

Through the side of the calorimeter head is soldered the copper tube by means of which hydrogen is led into the calorimeter. Inside the head it is bent so that the incoming hydrogen is directed down on to the surface of the liquid in the calorimeter.

When the calorimeter is in use, the glass portion is immersed almost up to the ground-glass joint in a water thermostat (temperature 29.3°) kept constant to 0.003°.

The thermometer is a 3-lead platinum resistance thermometer of the type described by C. H. Meyers,[2] in which the resistance element is only about 3 cm. long. It is filled with helium to ensure better thermal contact with the surroundings. The Wheatstone bridge used in connection with the thermometer is of the Mueller[3] type, and is enclosed in an air thermostat (temperature 30.0°) kept constant to 0.1°.

The electrical heater closely resembles the platinum resistance thermometer in design, a helix of constantan (B. & S. 34) instead of platinum being wound on the mica cross, and there being four leads—two current and two potential—of silk-covered copper wire (B. & S. 30) bound together and impregnated with cellulose acetate; total resistance 62 ohms.

The voltage across and the current through the heater are determined in the usual way by means of a potential divider, a standard resistance, and a potentiometer.

The Hydrogen Line.—Hydrogen[4] from a low pressure tank is purified and wetted. It is then passed into a measuring water buret of about 1 liter capacity, calibrated in cc., and suitably jacketed. The space above the water in the leveling bulb of the buret is also filled with hydrogen to prevent any gas other than hydrogen from getting into the buret. Before entering the calorimeter, the hydrogen from the buret is dried by passing through a tube containing "Dehydrite."

Procedure

Filling of the Ampoules.—For liquids an ampoule with a long thin neck, bent over in the form of a hook, is used.

(2) Meyers, *Bur. Standards J. Research*, **9**, 807 (1932).

(3) Mueller, *Bull. Bur. Standards*, **13**, 547 (1917).

(4) Electrolytic hydrogen of Ohio Chem. and Mfg. Co.

It is filled with nitrogen, and the liquid introduced by alternately warming and cooling the ampoule with the end of the neck under the liquid. It is finally cooled in dry-ice in an atmosphere of carbon dioxide, and the neck drawn off. With solids an ampoule with a thick-walled neck of small bore is employed. After the solid has been introduced, the ampoule is attached to a vacuum pump and sealed off. In both cases the difference in the weight of the ampoule before and after filling gives the weight of the substance to be hydrogenated or dissolved.

Hydrogenation Run.—The calorimeter is assembled with the ampoule held in the clip, and with catalyst and just sufficient solvent to cover the ampoule in the dewar flask. After evacuation, the calorimeter is filled with hydrogen from the measuring buret, and shaking and stirring are started. When the reduction of the catalyst (hydrated platinum oxide or palladium oxide) is complete, the temperature of the calorimeter is noted at intervals and, when the rate of heating has become constant, the temperature and volume (under atmospheric pressure) of the hydrogen in the measuring buret and the atmospheric pressure are noted. The ampoule is then broken, and the hydrogenation begins. This must be done as soon as possible after the catalyst has been completely reduced, as it is found that if the catalyst is left in the solution in the reduced state its activity decreases.

Throughout the reaction the pressure of hydrogen in the calorimeter is kept slightly greater than atmospheric. Temperature measurements are made at intervals until the reaction is complete, and the temperature–time curve is once more linear. The temperature and volume of the hydrogen in the measuring buret and the atmospheric pressure are once more noted. The volume of hydrogen absorbed can then be calculated, allowance being made for the fact that the gas in the buret is saturated with water vapor, and the completeness of the reaction can be checked.

Heat of solution run is similar to a hydrogenation run, but no catalyst is used, and no volume measurements are taken.

Calibration run is made immediately after the corresponding hydrogenation or solution run. The calorimeter is stirred and shaken and, when the rate of heating is constant, the calorimeter heater is switched on, and the time noted. The voltage across the heater is chosen so that the rate of increase of temperature of the calorimeter is approximately the same as in the corresponding hydrogenation run.

Temperature, voltage and current measurements are made at intervals, the averages of these sets of voltage and current readings being used in the computation of the electrical equivalent. When the temperature has risen approximately the same amount as in the hydrogenation run, the heater is switched off, the time being noted, and temperature readings continued until the temperature–time curve is once more linear.

Preparation and Purification of Materials

Substances Hydrogenated

n-**Heptene-1.**—The very pure product used was kindly supplied by Professor G. B. Kistiakowsky, and was a portion of the same sample he and his co-workers used in their gas-phase measurements [1]

1,4-Dihydronaphthalene.—A crude sample, supplied by du Pont de Nemours & Co., was purified by Straus and Lemmel's[5] modification of Sand and Genssler's[6] method. A further purification by fractional freezing was carried out; m. p. 24.5° (sharp).

1,2-Dihydronaphthalene.—This was obtained from 1,4-dihydronaphthalene by the method of Straus and Lemmel modified according to Straus,[7] and Straus and Lemmel;[8] m. p. −6.2° (sharp).

Methyl *cis*-**Cinnamate.**—The material used was kindly supplied by Dr. W. R. Smith, and was a portion of the same sample that he used in his work on the "Kinetics of Thermal *cis–trans* Isomerization";[9] m. p. −3.5° (sharp).

Methyl *trans*-**Cinnamate.**—Kahlbaum cinnamic acid was treated with methyl alcohol in the presence of concentrated sulfuric acid according to the method of Fischer and Speier;[10] m. p. 34.0° (sharp).

Isostilbene.—The sample was part of that used in the work on the "Kinetics of Thermal *cis–trans* Isomerization";[11] b. p. 145° (10 mm.).

Stilbene.—Eastman Kodak Co. product was purified by two crystallizations from 95% alcohol, followed by two crystallizations from absolute alcohol; m. p. 123.0° (sharp).

Diethyl Maleate.—Eastman Kodak Co. product was fractionally distilled three times under reduced pressure; b. p. 120.0° (25 mm.)

Diethyl Fumarate.—Eastman Kodak Co. product was fractionally distilled twice under reduced pressure; b. p. 115.0° (25 mm.).

1,4-Diphenylbutadiene.—The sample used was prepared by Dr. R. F. Jacobsen of Harvard University, according to the method of Thiele,[12] as improved by Kuhn and Winterstein;[13] m. p. 147–148°.

The percentage purity of each of these samples used for hydrogenation was ascertained by hydrogenating it and comparing the volume of hydrogen used with the theoretical volume required. The purities to within ±0.1% were found to be: *n*-heptene-1, 100%; 1,4-dihydronaphthalene, 93.1%; 1,2-dihydronaphthalene, 99.2%; methyl *cis*-cinnamate, 97.2%; methyl *trans*-cinnamate, 100%; *iso*-stilbene, 94.6%; stilbene, 100%; diethyl maleate, 100%; diethyl fumarate, 99.2%; diphenylbutadiene, 100%. In the calculations allowance has been made for the impurities where present.

Substances for Heat of Solution Measurements.—*n*-**Heptane, tetrahydronaphthalene, dibenzyl and diethyl succinate** were Eastman Kodak Co. products.

Methyl Hydrocinnamate.—Eastman Kodak Co. hydrocinnamic acid was esterified according to the method of Weger;[14] b. p. 230–232° (762.8 mm.).

Solvents.—Eastman Kodak Co. commercial decahydronaphthalene was stirred for twelve hours with concentrated sulfuric acid, and then with potassium per-

(5) Straus and Lemmel, *Ber.*, **46**, 236 (1913).
(6) Sand and Genssler, *ibid.*, **36**, 3706 (1903).
(7) Straus, *ibid.*, **46**, 1053 (1913).
(8) Straus and Lemmel, *ibid.*, **54**, 37 (1921).
(9) Kistiakowsky and Smith, THIS JOURNAL, **57**, 269 (1935).
(10) Fischer and Speier, *Ber.*, **28**, 3254 (1895).
(11) Kistiakowsky and Smith, THIS JOURNAL, **56**, 638 (1934).
(12) Thiele, *Ann.*, **306**, 198 (1899).
(13) Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 103 (1928).
(14) Weger, *Ann.*, **221**, 77 (1883).

manganate for an additional six hours. This last process produced a colloidal solution of the reagent in decahydronaphthalene and so the solution was stirred with acidified ferrous sulfate until colorless. The material was then washed several times with water, dried over anhydrous sodium sulfate, and fractionally distilled, a mixture of *cis*- and *trans*-forms being obtained; b. p. 187–190° (762.3 mm.).

95% Alcohol and absolute alcohol were Commercial Solvents Co. products.

n-Butyl Alcohol.—A good commercial sample was fractionated through a 9-foot column, and the middle fraction, boiling over a 0.1° range, used.

Cyclohexanol.—Eastman Kodak Co. pure product was employed.

Catalysts

PtO$_2$·H$_2$O.—This was prepared from platinum by the method of Adams, Voorhees and Shriner,[15] potassium nitrate, however, being used for the fusion instead of sodium nitrate as it was found that this gave a more active catalyst.

PdO was prepared from palladium by the method of Shriner and Adams.[16]

Test of Calorimeter

For the purpose of testing the accuracy of the results given by the calorimeter, the heat of hydrogenation of *n*-heptene-1 was investigated, as a very accurate value for this has been obtained by Kistiakowsky and his co-workers[1] by the vapor method. The choice of a suitable solvent in which to carry out the hydrogenations, however, caused some difficulty.

A liquid was required (a) which would be unaffected under the conditions of the experiments; (b) in which the hydrogenations would proceed to completion sufficiently quickly to make the correction for heat exchange with the surroundings small; (c) in which both the starting materials and the final products were soluble; and (d) which had a low vapor pressure, so that errors due to vaporization of the solvent would be minimized.
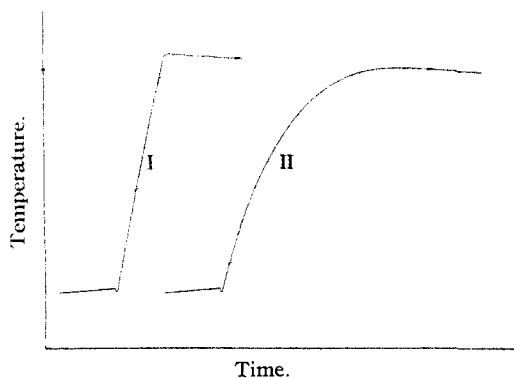

Fig. 2.

It was originally hoped to use decahydronaphthalene, as this has a very low vapor pressure at 29°, the temperature at which the hydrogenations were conducted, but this did

(15) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, p. 452.

(16) Shriner and Adams, THIS JOURNAL, 46, 1683 (1924).

not satisfy condition (b), very little hydrogen being absorbed. The same was true of cyclohexanol. As the work of Adams and his co-workers,[16] had shown that using as catalyst platinum or palladium prepared by the methods given above, the catalytic hydrogenation of aliphatic compounds as a general rule goes quickly in 95% ethyl alcohol, it was thought that *n*-butyl alcohol, with a lower vapor pressure than ethyl alcohol, would prove a suitable solvent, but this also was found to be unsatisfactory. 95% Ethyl alcohol and absolute ethyl alcohol were next tried, but when *n*-heptene-1 was hydrogenated in these solvents, less hydrogen than the theoretical quantity was taken up. Finally glacial acetic acid was tried, a solvent which had been found by Adams and his co-workers[15,16] to be very suitable for catalytic hydrogenations. In the present work, too, it proved to satisfy all the necessary conditions. When platinum was used as catalyst, however, the volume of hydrogen taken up in the hydrogenation of *n*-heptene-1 was 1 to 2% greater than the theoretical volume, while the values obtained for the heat of hydrogenation of this compound were high as compared with the gas phase values. Similar results were obtained in the hydrogenation of diethyl maleate with platinum as catalyst. The cause of this excess absorption of hydrogen is unknown, but it is apparently concerned somehow with the platinum catalyst, as in the case of the hydrogenation of both *n*-heptene-1 and of diethyl maleate this excess absorption was not noticed when palladium was used (see Tables I–IV). No excess absorption was observed in the hydrogenation of 1,2- and 1,4-dihydronaphthalenes with platinum as catalyst (see "Results"). It appears as if the reduction of the heptene or diethyl maleate caused the reduction of the catalyst, which for some reason had stopped, to go to completion. This interpretation would also account for the high heat values obtained with platinum; ΔH, roughly speaking, being larger, the greater the excess absorption. In this connection it may be mentioned that it was noticed that if the hydrogenatable material was present when the catalyst was being reduced, the hydrogenation of the material always took place more quickly than if the catalyst were reduced first and the hydrogenatable material introduced afterward, the simultaneous reduction of the catalyst stimulating the reduction of the other substance. In the case considered above something similar may be taking place, with the catalyst and the hydrogenatable material exchanging roles.

Another factor dependent on the catalyst employed is the shape of the temperature–time curve for the hydrogenation. When platinum is used, this curve has the general shape I (Fig. 2), but, when palladium is used, it is of type II. The initial drop in temperature observable in both cases when the ampoule is broken, is due to the heat absorbed on the solution of the reactant. A correction made for the heat of solution of the hydrogenation product compensates for this.

The results given in Tables I and II are for the hydrogenation of *n*-heptene-1 in glacial acetic acid as solvent, with platinum and palladium, respectively, as catalyst. The heats of hydrogenation, ΔH, apply to the reaction: *n*-Heptene-1(liquid) + Hydrogen(gas) → *n*-Heptane (dis-

solved). Tables III and IV contain similar results for the hydrogenation of diethyl maleate in glacial acetic acid. Table V contains the values determined for the heat of solution of n-heptane in glacial acetic acid, the results in each of the five tables being given in the order in which they were obtained. The heptene and heptane measurements were carried out at 29.1° and the diethyl maleate experiments at 29.3°, while the volume

TABLE I
HEPTENE HYDROGENATION

Heptene, g.	PtO₂·H₂O, g.	H₂ for hydrogenation, cc.		Excess in cc. of actual over theoretical	− ΔH, at 302°K., in cal./mole
		Theoretical	Actual		
1.2696	0.2	290	298	8	29,308
1.3953	.2	319	326	7	29,559
1.5491	.2	354	356	2	29,044
1.2031	.2	275	277	2	28,911
1.3347	.1	305	314	9	29,393

TABLE II
HEPTENE HYDROGENATION

Heptene, g.	PdO, g.	H₂ for hydrogenation, cc.		Excess in cc. of actual over theoretical	− ΔH, at 302°K., in cal./mole
		Theoretical	Actual		
1.2466	0.2	285	285	0	28,212
1.0388	.2	237	237	0	28,158
1.2885	.2	294	294	0	28,470

Average value of − ΔH = 28,280 ± 127 cal./mole.

TABLE III
DIETHYL MALEATE HYDROGENATION

C₆H₁₂O₄, g.	PtO₂·H₂O, g.	H₂ for hydrogenation, cc.		Excess in cc. of actual over theoretical	− ΔH, at 302°K., in cal./mole
		Theoretical	Actual		
2.2584	0.2	294	305	11	34,826
2.3807	.1	310	319	9	34,632
2.3158	.1	301	308	7	34,449
2.5204	.2	328	337	9	34,776
2.3899	.1	311	320	9	34,614
2.2390	.1	291	301	10	34,830
1.7496	.1	228	235	7	35,027

TABLE IV
DIETHYL MALEATE HYDROGENATION

C₆H₁₂O₄, g.	PdO, g.	H₂ for hydrogenation, cc.		Excess in cc. of actual over theoretical	− ΔH, at 302°K., in cal./mole
		Theoretical	Actual		
2.1909	0.2	285	285	0	33,042
2.0623	0.2	269	269	0	33,345

Average value of − ΔH = 33,193 ± 152 cal./mole.

TABLE V
HEAT OF SOLUTION OF HEPTANE

n-Heptane, g.	L_s, at 302°K., in cal./mole
1.3072	1439
1.5120	1428
1.1648	1442

Average value of L_s = 1436 ± 6 cal./mole.

of glacial acetic acid used in each run was 430 cc. All gaseous volumes are referred to S. T. P.

To obtain a value for the heat of hydrogenation of n-heptene-1 in the gas phase at 29.1°, the heats of vaporization of n-heptene-1 and of n-heptane at this temperature are also required. Bent and his co-workers[17] have measured the vapor pressure of n-heptene-1 at temperatures between 0.1 and 88.8°, and the slope of the straight line obtained by plotting log p against $1/T$ yields a value of 8100 ± 100 cal./mole for the heat of vaporization of n-heptene-1. This is taken as the value at 44.4°, the middle of the temperature range over which the measurements were conducted. Mathews[18] has determined the heat of vaporization of n-heptane directly, and has obtained a value of 7643 ± 4 cal./mole at 97.5°. On correcting the results to apply to 29.1°, which can be done by making use of the relationship

$$\frac{dL}{dT} = {}_gC_v - {}_lC_v + R - \frac{\alpha^2 TV}{\beta} \qquad (3)$$

where

All at T, °K.
$\begin{cases} L \text{ is the molar latent heat of vaporization} \\ {}_gC_v \text{ and } {}_lC_v \text{ are the heat capacities of the vapor and liquid, respectively, at constant volume} \\ \alpha \text{ is the coefficient of cubical expansion of the liquid} \\ \beta \text{ is the coefficient of compressibility of the liquid} \\ V \text{ is the molal volume of the liquid} \\ R \text{ is the gas constant} \end{cases}$

A value of 257 ± 152 cal. is obtained for the difference between the molar latent heats of vaporization of n-heptene-1 and n-heptane at 29.1°.

For the hydrogenation of n-heptene-1 in glacial acetic acid at 29.1° with palladium as catalyst, we therefore have for the terms in Eq. (1)

$$\Delta H_g = \Delta H - (_xL_v - {}_yL_v) - L_s$$

the values

$$\Delta H = -28,280 \pm 127 \text{ cal.}$$
$$(_xL_v - {}_yL_v) = + \quad 257 \pm 152 \text{ cal.}$$
$$L_s = + \quad 1436 \pm \quad 6 \text{ cal.}$$

Hence for ΔH_g, the heat of hydrogenation of n-heptene-1 in the gas phase at 29.1° (302.2°K.), we obtain the value

$$(-28,280 \pm 127) - (257 \pm 152) - (1436 \pm 6) = -29,973 \pm 285 \text{ cal./mole}$$

Assuming ΔC_p for the hydrogenation of n-heptene-1 to be the same as for the hydrogenation of ethylene, viz. −4.2 cal./degree⁻¹, the value obtained for the heat of hydrogenation of n-hep-

(17) Bent, et al., THIS JOURNAL, 58, 165 (1936).
(18) Mathews, ibid., 48, 562 (1926).

tene-1 in the gas phase at 355.1°K. is $-30,195 \pm 285$ cal./mole. The value yielded by the direct gas phase measurements at this temperature is $-30,137 \pm 37$ cal./mole.[1] The agreement is well within the experimental error, and is better than could be expected, as the values employed for the latent heats of vaporization of n-heptene-1 and of n-heptane in the conversion of the solution results to apply to the gas phase are somewhat uncertain, while the assumption that ΔC_p has the same value for the hydrogenation of n-heptene-1 as for the ethylene reaction may also introduce a substantial error. In the light of these considerations, the agreement is certainly close enough to prove the essential applicability of the solution method employed, when palladium is used as catalyst. When platinum is used, however, the results are sometimes not satisfactory, as too much hydrogen is absorbed, causing high values to be obtained for the heat of hydrogenation (see Tables I and III).

If the latent heat of vaporization corrections and the temperature correction are not made, we have as the heat of the reaction

n-Heptene-1(liquid) $+$ Hydrogen(gas) $\longrightarrow$ n-Heptane (liquid) at 29.1°

$(-28,280 \pm 127) - (1436 \pm 6) = -29,716 \pm$
133 cal./mole
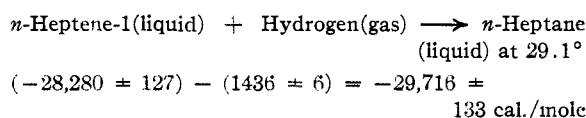
The precision of the actual measurements is therefore about $1/2\%$, but it is difficult to estimate the over-all error; it is probably not more than 1%.

Results

All measurements were made at 29°, 430 cc. of glacial acetic acid being used as solvent in each case; 0.2 g. of PdO was used as catalyst in each hydrogenation, except where otherwise stated. The final value, ΔH_1, given for each heat of hydrogenation with the exception of the heat of hydrogenation of 1,4-diphenylbutadiene-1,3, applies to the reaction

X(liquid) $+$ Hydrogen(gas) $\longrightarrow$ Y(liquid)
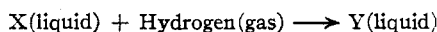
at the temperature of the measurements. In the case of the diphenylbutadiene, the value ΔH_d given applies to the reaction

Diphenylbutadiene(dissolved) $+$ H_2(gas) $\longrightarrow$
Diphenylbutane(dissolved)
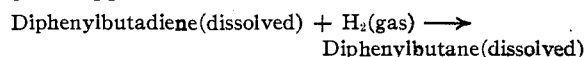
The latent heat of fusion values required have been taken from the literature.

Hydrogenation of 1,4-Dihydronaphthalene and 1,2-Dihydronaphthalene to Tetrahydronaphthalene.—In these hydrogenations, platinum was

used as catalyst, as with palladium the reactions did not proceed to completion. No excess absorption of hydrogen was noticed in these cases.

TABLE VI
HYDROGENATION OF 1,4-DIHYDRONAPHTHALENE

$C_{10}H_{10}$, g.	$PtO_2 \cdot H_2O$, g.	H_2 for hydrogenation, cc. Theoretical	Actual	$-\Delta H$, at 302°K., in cal./mole
1.5134	0.4	261	262	26,399
1.7434	.3	300	300	26,126
2.1606	.2	372	371	26,306

Average value of $-\Delta H = 26,277 \pm 101$ cal./mole.

TABLE VII
HYDROGENATION OF 1,2-DIHYDRONAPHTHALENE

$C_{10}H_{10}$, g.	$PtO_2 \cdot H_2O$, g.	H_2 for hydrogenation, cc. Theoretical	Actual	$-\Delta H$, at 302°K., in cal./mole
1.5335	0.2	264	264	23,133
1.7383	.2	299	299	23,707
1.7786	.1	306	306	23,552

Average value of $-\Delta H = 23,254 \pm 199$ cal./mole.

TABLE VIII
SOLUTION OF TETRAHYDRONAPHTHALENE

$C_{10}H_{12}$, g.	L_s, at 302°K., in cal./mole
1.7294	845
1.8209	844

Average value of $L_s = 844 \pm 0$ cal./mole.

Therefore for 1,4-dihydronaphthalene at 302°K., $\Delta H_1 = \Delta H - L_s = -27,121 \pm 101$ cal./mole; and for 1,2-dihydronaphthalene at 302°K., $\Delta H_1 = \Delta H - L_s = -24,098 \pm 199$ cal./mole.

Hydrogenation of Methyl cis-Cinnamate and Methyl trans-Cinnamate to Methyl Hydrocinnamate.

TABLE IX
HYDROGENATION OF METHYL cis-CINNAMATE

$C_{10}H_{10}O_2$, g.	H_2 for hydrogenation, cc. Theoretical	Actual	$-\Delta H$, at 302°K. in cal./mole
1.7905	248	250	28,126
2.0142	278	278	27,668
2.1522	297	296	27,524

Average value of $-\Delta H = 27,773 \pm 236$ cal./mole.

TABLE X
HYDROGENATION OF METHYL trans-CINNAMATE (SOLID)

$C_{10}H_{10}O_2$, g.	H_2 for hydrogenation, cc. Theoretical	Actual	$-\Delta H$, at 302°K., in cal./mole.
1.9524	270	271	19,496
2.2006	304	304	19,596
2.6403	365	365	19,322

Average value of $-\Delta H = 19,471 \pm 100$ cal./mole. L_f, molar latent heat of fusion $= 4295$ cal./mole.[19]

(19) "Handbook of Chemistry and Physics," 21st Edition. 1936-1937.

TABLE XI
SOLUTION OF METHYL HYDROCINNAMATE

$C_{10}H_{12}O_2$, g.	L_s, at 302°K., in cal./mole.
2.4108	415
2.5371	420

Average value of L_s = 417 ± 2 cal./mole.

Therefore for methyl cis-cinnamate at 302°K., $\Delta H_l = \Delta H - L_s = -28,190 \pm 238$ cal./mole; and for methyl $trans$-cinnamate at 302°K., $\Delta H_l = \Delta H - L_s L_f = -24,183 \pm 102$ cal./mole.

Hydrogenation of i-Stilbene and Stilbene to Dibenzyl.

TABLE XII
HYDROGENATION OF i-STILBENE

$C_{14}H_{12}$, g.	H_2 for hydrogenation, cc. Theoretical	Actual	$-\Delta H$, at 302°K., in cal./mole.
1.2465	155	157	25,761
1.4883	185	185	25,328
1.8863	235	234	25,732

Average value of $-\Delta H$ = 25,607 ± 186 cal./mole.

TABLE XIII
HYDROGENATION OF STILBENE (SOLID)

$C_{14}H_{12}$, g.	H_2 for hydrogenation, cc. Theoretical	Actual	$-\Delta H$, at 302°K. in cal./mole.
0.9633	120	121	12,736
1.0117	126	127	12,776

Average value of $-\Delta H$ = 12,756 ± 20 cal./mole. $_xL_t$, molar latent heat of fusion, 7186 cal./mole.[19]

TABLE XIV
SOLUTION OF DIBENZYL

$C_{14}H_{14}$, g.	L_s, at 302°K., in cal./mole.
0.9757	5855
1.1045	5824

Average value of L_s = 5839 ± 16 cal./mole. $_yL_t$, molar latent heat of fusion = 5645 cal./mole.[19]

Therefore for i-stilbene at 302°K., $\Delta H_l = \Delta H - L_s + {_yL_f} = -25,801 \pm 202$ cal./mole, and for stilbene at 302°K., $\Delta H_l = \Delta H - L_s - {_xL_f} + {_yL_f} = -20,136 \pm 36$ cal./mole.

Hydrogenation of Diethyl Maleate and Diethyl Fumarate to Diethyl Succinate

Hydrogenation of Diethyl Maleate.—These results already have been given in Table IV, average value of $-\Delta H$ = 33,193 ± 152 cal./mole.

TABLE XV
HYDROGENATION OF DIETHYL FUMARATE

$C_8H_{12}O_4$, g.	H_2 for hydrogenation, cc. Theoretical	Actual	$-\Delta H$, at 302°K. in cal./mole.
1.9989	260	260	29,124
2.0848	271	272	28,830

Average value of $-\Delta H$ = 28,977 ± 147 cal./mole.

TABLE XVI
SOLUTION OF DIETHYL SUCCINATE

$C_8H_{14}O_4$, g.	L_s, at 302°K., in cal./mole.
1.9197	327
2.7890	325

Average value of L_s = 326 ± 1 cal./mole.

Therefore for diethyl maleate at 302°K., $\Delta H_l = \Delta H - L_s = -33,519 \pm 153$ cal./mole; and for diethyl fumarate at 302°K., $\Delta H_l = \Delta H - L_s = -29,303 \pm 148$ cal./mole.

Hydrogenation of 1,4-Diphenylbutadiene to 1,4-Diphenylbutane.

TABLE XVII
HYDROGENATION OF 1,4-DIPHENYLBUTADIENE

$C_{16}H_{14}$, g.	H_2 for hydrogenation, % Theoretical	Actual	$-\Delta H$, at 302°K. in cal./mole.
1.1138	242	243	38,306
1.4421	314	315	38,038

Average value of $-\Delta H$ = 38,172 ± 134 cal./mole.

TABLE XVIII
SOLUTION OF 1,4-DIPHENYLBUTADIENE

$C_{16}H_{14}$, g.	L_s, at 302°K., in cal./mole.
0.6223	5853
0.6770	5881

Average value of L_s = 5867 ± 14 cal./mole.

Therefore for 1,4-diphenylbutadiene at 302°K., $\Delta H_d = \Delta H - L_s = -44,039 \pm 148$ cal./mole.

Discussion of Results

The figures deduced above for the heats of hydrogenation apply to the liquid state at 29°, except in the case of diphenylbutadiene, where the value applies to the dissolved state at the same temperature. To consider them in relation to those of Kistiakowsky and his co-workers,[1] they have to be made to apply to the gas state at 82°, a correction which involves in all cases a knowledge (1) of the heats of vaporization of reactant and hydrogenated product, and (2) of ΔC_p for the reaction concerned. In the case of diphenylbutadiene, the heats of solution and fusion of the reactant and product must be known in addition. Unfortunately none of the values required is available, and so it is assumed that the correction in each case amounts to -0.5 kcal., its magnitude in the case of the hydrogenation of n-heptene-1 (see "test of calorimeter"). For the gas-phase addition of 1 mole of hydrogen at 82° we therefore have for ΔH_g:

	Kcal.
1,4-Dihydronaphthalene	−27.6
1,2-Dihydronaphthalene	−24.6
Methyl *cis*-cinnamate	−28.7
Methyl *trans*-cinnamate	−24.7
i-Stilbene	−26.3
Stilbene	−20.6
Diethyl maleate	−34.0
Diethyl fumarate	−29.8
1,4-Diphenylbutadiene	−44.5

The effect of substituents on the heat of hydrogenation of the ethylene double bond has been shown by Kistiakowsky and his co-workers[1] to be largely independent of the nature of the substituent, except where the substituent is such that conjugation with the double bond can take place, e. g., in crotonaldehyde, ethyl vinyl ether, 2-ethoxypropene, and to depend only on the number and position of the substituents. Thus ΔH_g at 82° for ethylene is −32.8 kcal., for $RCH=CH_2$ is −30.2 kcal., for $R_2C=CH_2$ is −28.2 kcal., for $CH_3CH=CHCH_3$ (*trans*) is −27.6 kcal. and for $CH_3CH=CHCH_3$ (*cis*) is −28.6 kcal. (the last two are isolated values) for $R_2C=CHR$ is −26.9 kcal., and for $R_2C=CR_2$ is −26.6 kcal. An examination of the present results in the light of these conclusions is interesting.

1,4-Dihydronaphthalene and diethyl fumarate might be expected to have the same heats of hydrogenation as cyclohexene and *trans*-butene-2, respectively, viz., −28.6 kcal. and −27.6 kcal. The values obtained are −27.6 kcal. and −29.8 kcal. The first is in good agreement, but the second is higher than expected. Again, the heat of addition of 1 mole of hydrogen to 1,2-dihydronaphthalene, methyl *trans*-cinnamate, and stilbene should be the same as the heat of hydrogenation of *trans*-butene-2, when allowance is made for conjugation of the side-chain double bond with the nucleus. The difference between the heats of hydrogenation of 1,4- and 1,2-dihydronaphthalenes, −27.6 and −24.6 kcal., gives the amount of conjugation in 1,2-dihydronaphthalene as 3.0 kcal.; the difference between the heats of hydrogenation of the esters of crotonic acid (*trans*), −28.2 kcal.,[20] and of methyl *trans*-cinnamate, −24.7 kcal., gives the amount of conjugation in methyl *trans*-cinnamate as 3.5 kcal. The observed heats of addition of 1 mole of hydrogen to 1,2-dihydronaphthalene and methyl *trans*-cinnamate are −24.6 kcal. and −24.7 kcal. If

(20) Schjänberg, Z. physik. Chem., 179A, 39 (1937). The value has been adjusted to make it comparable with the others under consideration.

there were no conjugation, the values would therefore be −27.6 kcal. and −28.2 kcal., both of which are in good agreement with the value for *trans*-butene-2, −27.6 kcal. In the case of stilbene, −20.6 kcal. was observed for the addition of 1 mole of hydrogen, which, on comparison with the value of −27.6 kcal. for *trans*-butene-2, yields a figure of 7.0 kcal. for the increased stability of the side-chain double bond in stilbene due to conjugation with both nuclei.

There are no data with which the values obtained for diethyl maleate, methyl *cis*-cinnamate, and *i*-stilbene can be compared. It might be noted here, however, that the heat of hydrogenation of diethyl maleate, −34.0 kcal., is even greater than that of ethylene, −32.8 kcal. This effect of the carboxyl group has already been noted by Kistiakowsky.[1]

There remains the value for 1,4-diphenylbutadiene-1,3, −44.5 kcal., to be considered. What is more interesting is the value of ΔH for the addition of 1 mole of hydrogen to give 1,4-diphenyl-*trans*-butene-2. No data are available for the heat of hydrogenation of this compound, but it may be taken to be the same as that of *trans*-butene-2, viz., −27.6 kcal. Hence ΔH for 1,4-diphenylbutadiene-1,3 to 1,4-diphenyl-*trans*-butene-2 is −16.9 kcal. The heats of hydrogenation of butadiene-1,3 (−57.1 kcal.) and of *trans*-butene-2 (−27.6 kcal.) give ΔH for butadiene-1,3 to *trans*-butene-2 as −29.5 kcal. Before this figure can be compared with that for 1,4-diphenylbutadiene-1,3, it must be corrected for the effect of the introduction of two substituent groups in the 1,4 positions. The magnitude of this effect may be taken as the difference between the heats of hydrogenation of ethylene (−32.8 kcal.) and of *trans*-butene-2 (−27.6 kcal.), viz., + 5.2 kcal. The calculated value for the addition of 1 mole of hydrogen to 1,4-diphenylbutadiene-1,3 is therefore −24.3 kcal., and the difference between this and the observed value, −16.9 kcal., viz., 7.4 kcal., is due to the conjugation of the side-chain double bonds with the nuclei. This value may be compared with the value of 7.0 kcal. obtained for the increased stability of the side-chain double bond in stilbene due to conjugation with the nuclei present. The total increase in stability in 1,4-diphenylbutadiene-1,3, due to conjugation of the double bonds, not only with the nuclei, but also with each other, is given by the difference in the heats of addition of 1 mole of hydrogen to 1,4-

diphenylbutadiene-1,3 and to 1,4-diphenyl-*trans*-butene-2, *viz.*, 10.7 kcal.

From their results, Kistiakowsky and his co-workers[1] have evaluated in many cases the increase in stability of a compound due to conjugation. Except in benzene (36.0 kcal.) and furan (17.2 kcal.), this increase in stability never exceeds 4 kcal. As has been mentioned above, the present investigation yields for this increase in stability a value of 3.0 kcal. for 1,2-dihydronaphthalene; 3.5 kcal. for methyl *trans*-cinnamate and presumably also for methyl *cis*-cinnamate; 7.0 kcal. for stilbene and presumably also for *i*-stilbene; and 10.7 kcal. for 1,4-diphenylbutadiene-1,3. The first two of these results fall into line, while the last two, taken in conjunction with the fact that the conjugation between the side-chain and the nucleus in styrene amounts to 1.6 kcal., indicate that the presence of a second phenyl group which can conjugate with the double bonds in a chain greatly increases the stability. No compound of this type was among those studied by Kistiakowsky. Again the fact that ΔH for diethyl fumarate (-29.8 kcal.) is greater than ΔH for *trans*-butene-2 (-27.6 kcal.) confirms the conclusions of Kistiakowsky and his co-workers[1] that there is no conjugation in a system of the type $\mathrm{>C{=}C{-}C{<}^{O-R}_{O}}$.
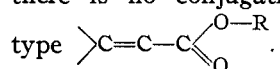
The results of these workers on cyclopentene, cyclohexene, cyclopentadiene, cyclohexadiene, hydrindene, and *o*-xylene indicate that the 5-membered-ring compound always has a lower heat of hydrogenation than the corresponding 6-membered-ring compound (the value for *o*-xylene was taken as the value for tetralin, the uninvestigated 6-membered-ring compound corresponding to hydrindene). The differences for the above pairs of compounds are 1.7, 4.5 and 1.5 kcal., respectively, and have been taken to indicate that whereas all 6-membered rings, saturated or unsaturated, are strainless, the strain in a 5-membered ring increases with increasing saturation. From the heat of hydrogenation of 1,2-dihydronaphthalene to tetralin obtained in the present investigation, *viz.*, -24.6 kcal., the heat of the complete hydrogenation of the dihydronaphthalene to decalin can be calculated by adding the heat of hydrogenation of *o*-xylene, *viz.*, -47.3 kcal. The value obtained is -71.9 kcal., while that for indene, the corresponding 5-membered-ring compound, is -69.9 kcal. In this case also,

therefore, the heat of hydrogenation of the 5-membered-ring compound is less than that of the 6-membered-ring compound to the extent of 2 kcal.

Values for the molar heats of isomerization of 1,4-Dihydronaphthalene → 1,2-Dihydronaphthalene, of Methyl *cis*-Cinnamate → Methyl *trans*-Cinnamate, of Diethyl Maleate → Diethyl Fumarate, and of *i*-Stilbene → Stilbene, are directly obtainable from the determined heats of hydrogenation of these substances. The values yielded for the liquid → liquid isomerizations are -3.0, -4.0, -4.2 and -5.7 kcal., respectively. As in the case of heats of hydrogenation, there are very few figures with which these values can be compared, because heats of isomerization have previously been obtained chiefly as the small differences between the large and uncertain values available for the heats of combustion of the isomers in question. Kistiakowsky and Smith[11] have, however, by observation of the equilibrium in the gaseous system stilbene—*i*-stilbene, obtained the value of -3.0 kcal. for the molar heat of isomerization of gaseous *i*-stilbene → gaseous stilbene at about 300°, a value appreciably lower than that obtained in the present investigation. As the number of pairs of geometrical isomers for which the heat of isomerization is accurately known is so small, no attempt can be made to correlate the heat of isomerization with molecular structure.

Summary

1. A calorimeter and technique for measuring the heats of catalytic hydrogenations in solutions at room temperature with a precision of the order of 0.5%, are described.

2. The accuracy of the results yielded by the method has been proved by determining the heat of hydrogenation of *n*-heptene-1 in glacial acetic acid at 302°K., and comparing the value for the gaseous hydrogenation at 355°K., derived from these solution measurements, with that obtained directly by Kistiakowsky and his co-workers.

3. The following heats of addition of 1 mole of hydrogen have been obtained at 302°K.

	ΔH in cal./mole.
1,4-Dihydronaphthalene	−27,121 ± 101
1,2-Dihydronaphthalene	−24,098 ± 199
Methyl *cis*-cinnamate	−28,190 ± 238
Methyl *trans*-cinnamate	−24,183 ± 102
i-Stilbene	−25,801 ± 202
Stilbene	−20,136 ± 36
Diethyl maleate	−33,519 ± 153
Diethyl fumarate	−29,303 ± 148
1,4-Diphenylbutadiene	−44,039 ± 148

The values apply to the reactions X(liquid) + H_2(gas) → Y(liquid), except in the case of 1,4-diphenylbutadiene, where the value applies to the reaction X(dissolved in glacial acetic acid) + H_2(gas) → Y(dissolved in glacial acetic acid).

4. These results have been found to agree with the rules put forward by Kistiakowsky for the effect of substituents on the heat of hydrogenation of the ethylenic double bond.

5. Values have been obtained for the increase in stability, due to conjugation, of certain of the compounds investigated, and the heats of isomerization of the pairs of stereoisomers considered.

6. The heat of complete hydrogenation of 1,2-dihydronaphthalene has been shown to be greater than that for indene, the corresponding 5-membered-ring compound, in agreement with results previously obtained by Kistiakowsky and his co-workers for other similar pairs of compounds.

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Studies in Gaseous Hydrogenation and Polymerization Reactions[1]

BY HUGH D. BURNHAM[2] AND ROBERT N. PEASE

Earlier work from this and other laboratories has led to the now quite generally accepted conclusion that the decomposition of many organic compounds occurs in part, at least, through reactions of the chain type.[3] One of the most effective methods of demonstrating the presence of reaction chains has been to observe the rate of decomposition in the presence and absence of small quantities of nitric oxide. Apparently nitric oxide is capable of reacting with the type of chain carriers found in pyrolysis of the paraffins, ethers and of some aldehydes[4] so that a lower reaction rate in the presence of nitric oxide is taken to indicate that part of the reaction at least occurs by chain type processes.

Since the inhibition by nitric oxide must affect both the forward and reverse reactions to an equivalent degree (otherwise the position of equilibrium must necessarily shift), it was to be anticipated that the hydrogenation of ethylene as well as the decomposition of ethane ($C_2H_6 \rightleftharpoons H_2 + C_2H_4$) must be inhibited by nitric oxide. A

preliminary communication on this subject already has appeared.[5] Further, it was believed that if the polymerization of ethylene could be inhibited to a greater extent than the hydrogenation reaction, then the hydrogenation could be studied over greater ethylene/hydrogen ratios than had heretofore been possible. Unfortunately, this has not been found to be the case, though polymerization is inhibited.

Experimental

Kinetic data were obtained from pressure measurements at constant volume, supplemented by analysis of residual gases. For the most part the apparatus was of a familiar type. The reaction bulb was a cylindrical Pyrex glass vessel 3.5 cm. in diameter and 22 cm. long. The method of mounting the bulb in the specially constructed furnace and the photoelectric thermostat control are the same as previously used in this Laboratory and described previously.[6]

Ethylene and propylene were obtained in commercial cylinders. The olefins were purified by repeated freezing out in liquid air and pumping off the residual gases. On warming up, the first portions were discarded and middle portions stored for experiments. Acetylene was obtained from a Prest-O-lite cylinder in which the gas is dissolved in acetone. The gas was passed through a calcium chloride tower. Subsequent purification was the same as that described for the olefins. Electrolytic hydrogen was further purified by passing over platinized asbestos at 300° and then through a liquid air trap to remove water.

(1) Abstracted from a thesis by Hugh D. Burnham, presented to the faculty of Princeton University, in partial fulfillment of the requirements for the Ph.D. degree, June, 1940.

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(3) Ethers: Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A159**, 192 (1937); Paraffins: Staveley, *ibid.*, **A162**, 557 (1937); Hobbs and Hinshelwood, *ibid.*, **A167**, 447 (1938); Echols and Pease, THIS JOURNAL, **61**, 1024 (1939).

(4) Staveley and Hinshelwood, *J. Chem. Soc.*, 1568 (1937).

(5) Burnham and Pease, THIS JOURNAL, **62**, 453 (1940).

(6) Echols and Pease, *ibid.*, **61**, 208 (1939).