HEATS OF HYDROGENATION

PART 1.—DODECA-3:9 AND -5:7 DIYNES

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A calorimeter suitable for the measurement of heats of hydrogenation of unsaturated hydrocarbons in solution is described. The calorimeter has a Pyrex reaction vessel immersed in water in a Dewar flask, and a novel feature is the attachment of the reaction vessel via an arm through the calorimeter lid to a mechanical " vibro-shaker ". This allowed violent agitation of the reactants in the reaction vessel, enabling the hydrogenation experiments to be brought to completion in 10-20 min.

Some measurements are reported on the heats of hydrogenation in solution of hexene-1, fumaric acid, maleic acid, dodeca-3 : 9-diyne, dodeca-5 : 7-diyne, and octa-1 : 7-diyne. The heat of hydrogenation of octa-1 : 7-diyne is close to that of *two* moles of 1-butyne, and the heat of hydrogenation of dodeca-3 : 9-diyne is close to that of *two* moles of 3-hexyne, indicating that in both these diynes there is very little interaction between the —C≡C— groups. The heat of hydrogenation of the conjugated dodeca-5 : 7-diyne is *ca.* 4 kcal/mole *less* than that of the 3 : 9-isomer. It is deduced from the experimental results that the overall conjugation energy of the system —C≡C—C≡C— is *ca.* 10 kcal/mole: a calculation of the conjugation energy by the method of Coulson and Crawford gives a value of *ca.* 12 kcal/mole.

Although a great deal of heat of formation data has been obtained on saturated and unsaturated hydrocarbons, little or no information is available on the heats of formation of diacetylenes and polyacetylenes. These compounds are not in general well-suited to study by bomb-combustion calorimetry, since they tend to detonate on ignition. A more promising route to their heats of formation would seem to be offered through heats of hydrogenation.

Heats of hydrogenation of several unsaturated hydrocarbons in the *vapour* phase have been accurately measured by Kistiakowsky and co-workers,[1] and Williams [2] has described a calorimeter suitable for the measurement of heats of hydrogenation in *solution*. Our preliminary studies on the heat of hydrogenation of 5 : 7 dodeca-diyne were made in a calorimeter similar to that of Williams, using 500-ml ethanol as solvent, and reduced PtO_2 as catalyst. We found, however, that the rate of hydrogenation at 25° C was inconveniently slow. The disadvantage of Williams' calorimeter stems from the usage of a conventional rotary stirrer, with which it is difficult—unless the heat of stirring becomes excessive—to attain a sufficient agitation of the reaction mixture.

The various factors influencing the rate of catalytic hydrogenation of olefines in the liquid phase have been examined by Watt and Walling,[3] who concluded that the controlling factor is the rate of diffusion of hydrogen to the catalyst surface. In this connection, they found mechanical shaking of the reaction mixture to be far more effective than rotary stirring, e.g., a faster reaction rate was achieved by shaking at 200 osc./min than by rotary stirring at 930 rev/min.

Accordingly, we designed a calorimeter in which a small reaction vessel is agitated at rates from 700 to 1000 osc./min by means of a vibroshaker. With this, a hydrogenation experiment could be completed in 10-15 min, as opposed to several hours in the Williams-type calorimeter.

EXPERIMENTAL

PREPARATION OF COMPOUNDS

Hexene-1 was a high purity sample provided by the C.R.L., Teddington.

Fumaric acid was a commercial sample, purified by repeated recrystallization from hot N hydrochloric acid solution.

Maleic acid was a commercial sample, recrystallized from petroleum ether+acetone solution.

Octa-1 : 7-diyne was prepared by reacting tetramethylene dibromide with sodium acetylide in liquid ammonia. A suspension of sodium acetylide (40 g sodium, 700 ml liquid ammonia) was prepared in the normal way in a 2-l. Dewar vessel, fitted with a dry-ice cooled reflux condenser. 100 g of the dibromide in 50 ml dry ether were added slowly, and the mixture left with stirring overnight. 10 g ammonium chloride were slowly added, followed by 400 ml water, and 250 ml ether. The contents of the Dewar flask were transferred to a separating funnel, and the ether layer separated. The aqueous layer was extracted with ether 3 times. The combined ether was washed with water, dilute acid, water, sodium bicarbonate solution, and then dried over anhydrous magnesium sulphate. The ether was removed by distillation through a Fenske column, and the crude product purified by fractional distillation under reduced pressure through an 8-in. gauze-packed column. The colourless fraction (b.p. 35·5 at 4 mm Hg) was retained : n_D^{20} = 1·4485.

Dodeca-5 : 7-diyne was prepared by the general method described by Armitage, Jones and Whiting,[4] starting from sodamide in liquid ammonia and 1 : 4-dichlorobut-2-yne, to which butyl bromide was subsequently added. The crude product was fractionally distilled under reduced pressure, and the fraction b.p. 70·1° C at 0·6 mm Hg, n_D^{20} = 1·4880, retained. The freshly distilled compound is colourless, but takes on a yellow to brown colour on standing.

Dodeca-3 : 9-diyne was prepared by reacting ethyl bromide with the disodium salt of octa-1 : 7-diyne. A suspension of sodamide in liquid ammonia (25 g sodium, 800 ml liquid ammonia) was prepared, and 50 g of octa-1 : 7-diyne added over a period of 3 h. 160 g ethyl bromide were then added in 2 h, and the reaction mixture left overnight. The mixture was treated with 15 g ammonium chloride, followed by 400 ml of water and 250 ml of ether. The ether layer was separated, and the aqueous layer ether extracted. The combined ether was washed with water, dilute hydrochloric acid, water, sodium bicarbonate solution, and then dried over magnesium sulphate. The ether was removed by distillation through a Fenske column, and the crude product purified by fractional distillation under reduced pressure. The fraction, b.p. 56·5° C at 0·5 mm Hg, n_D^{20} = 1·4650, was retained. The purified substance is a colourless liquid which, unlike the 5 : 7 isomer, remains colourless after long standing.

THE CALORIMETER

The calorimeter is a cylindrical silvered Dewar vessel, ¾-l. capacity, encased in a copper can fitted with a flanged brass lid, and, when in use, was totally immersed in a thermostat bath maintained at 25·0° C. The Pyrex glass reaction vessel entered the calorimeter centrally through a chimney in the calorimeter lid. It consisted of a cylindrical reaction chamber (*ca.* 25-ml capacity) sealed to a length of ½ in. tubing terminating in a B 19 socket (fig. 1). The reaction vessel was clamped below the cone-joint to the arm of a vibro-shaker. A rod of capillary tubing passing centrally through the B 19 cone, and reaching into the reaction chamber, served as the inlet for hydrogen, and also to support the ampoule containing the substance under investigation. Two further chimneys in the calorimeter lid allowed entrance of a shielded thermistor element (Stantel, F 2311/30), and a calibration heater. The latter was layer-wound of 35 s.w.g. double silk-covered wire (12·66 Ω per yd.) on a 3-mm brass rod, and firmly enclosed in a tight-fitting glass tube. The thermistor element was covered with aluminium foil to shield it, and was rigidly mounted in a close-fitting glass tube. The resistance of the thermistor element was measured by a Cambridge Wheatstone bridge of the decade type, used in conjunction with a short-period reflecting galvanometer.

In a hydrogenation experiment, the reaction vessel was charged with 10 or 15 ml solvent (alcohol, or acetic acid) and 0·1 g platinum oxide, or palladium oxide, catalyst. A glass ampoule containing a weighed amount of diacetylene was sealed to the capillary tube holder, and inserted into the reaction chamber. The charged reaction vessel was then positioned in the Dewar vessel, containing 375 g distilled water, and the whole calorimeter immersed in the thermostat bath. The vibro-shaker was set in motion, and the oscillation rate adjusted to give a satisfactory stirring performance in the calorimeter. The system was allowed time (usually *ca.* 30 min) to achieve a steady state.

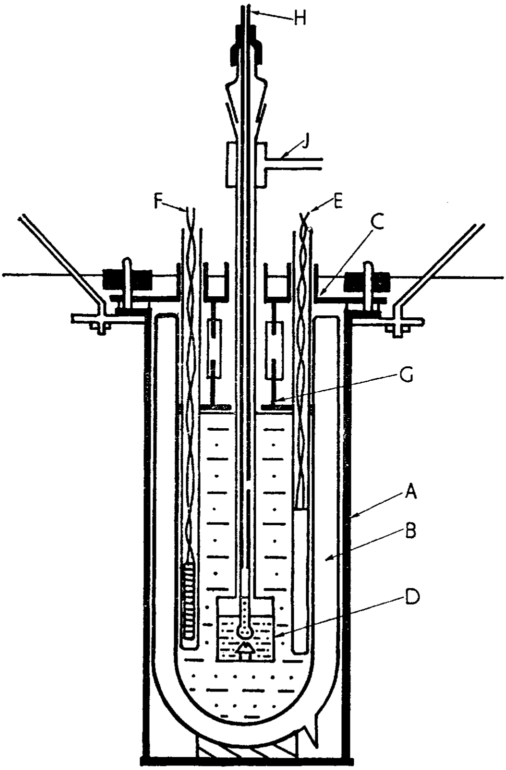

FIG. 1.

A, copper can;
B, Dewar vessel;
C, calorimeter lid;
D, Pyrex reaction vessel;
E, thermistor;
F, heater;
G, ceiling;
H, hydrogen inlet;
J, vibro-shaker arm.

The air in the reaction vessel was then pumped out (through the capillary tube inlet), and replaced by hydrogen from the gas burette. Reduction of the catalyst quickly took place, hydrogen being supplied continuously until no further absorption occurred. Following this, the thermistor resistance was plotted against time for a period of 20 min to establish the fore-rating characteristics. Now the ampoule in the reaction vessel was broken,* the time noted, and the initial volume of hydrogen read off in the burette. Thermistor readings, and hydrogen volume readings, were made at regular intervals during the ensuing reaction period, which was usually about 10-20 min. When the hydrogenation reaction ceased (no further absorption of hydrogen), the final hydrogen volume was noted, and resistance readings were taken for a further period of *ca.* 30 min at the end of the reaction, to establish the after-rating characteristics.

The false " ceiling " shown in fig. 1 may be noted. This rubber-backed copper disc was suspended by insulated rods from the flange top of the calorimeter, and rested just over the surface of the water in the Dewar vessel. Its purpose was to stop undue splashing of the calorimeter fluid, caused by the oscillation of the reaction vessel immersed in it.

CALIBRATION

The calorimeter was calibrated electrically by the substitution method. The calibration experiments were found to be reproducible within limits of ± ½ %: this performance is below the standard commonly attained with a submerged Dewar vessel calorimeter, stirred by a rotary stirrer. In our view, the performance of the present calorimeter could

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* The vibro-shaker was stopped for a few seconds during this operation.

be improved upon by replacing the variable speed vibro-shaker by one driven by a constant speed motor.

UNITS

All heat quantities are given in thermochemical calories, defined by 1 calorie ≡ 4·1840 abs. joules. The experiments were carried out at 25° C.

RESULTS

In order to test the suitability of the " shaking " calorimeter for hydrogenation studies, some measurements were made on the heats of hydrogenation of hexene-1, maleic acid, and fumaric acid.

HEXENE-1

In his heat of hydrogenation studied on olefines in solution, Williams [2] examined the effectiveness of two catalysts—reduced PtO_2 and reduced PdO—and of different solvents, in particular ethanol and glacial acetic acid. He pointed out that the uptake of hydrogen when reduced PtO_2 is used as catalyst is frequently in excess of the theoretical, but that reduced PdO catalyst is less prone to cause excess hydrogen absorption. Our experience has been similar, and for this reason most of the reductions were made with reduced PdO as catalyst. In the hydrogenation experiments on hexene-1, the uptake of hydrogen was found to exceed the theoretical by 1 or 2 % with Pd and by as much as 3 or 4 % with Pt catalyst. The heats of hydrogenation are therefore referred to the amount of hydrogen consumed, rather than to the weight of hexene added.

TABLE 1.—HEAT OF HYDROGENATION OF HEXENE-1

expt.	wt. hexene (g)	H_2 absorbed (cm³ at s.t.p.)	$-\Delta H_{\text{obs.}}$ (kcal/mole H_2)	catalyst
1	1·0095	271·0	29·16	Pd/HAc
2	0·8363	227·0	28·59	Pd/HAc
3	0·8610	238·2	28·68	Pt/HAc
4	0·5927	161·5	29·00	Pd/HAc

mean $\Delta H_{\text{obs.}} = -$ 28·85 ± 0·23 kcal/mole.

The observed heat of hydrogenation, $\Delta H_{\text{obs.}}$, refers to the formation of hexane in *solution* in the glacial acetic acid solvent. The heat of solution was measured independently, $\Delta H_{\text{soln.}} = 1\cdot25 \pm 0\cdot1$ kcal/mole, whence, for the reaction

$CH_3.CH_2.CH_2.CH_2.CH{=}CH_2\,(liq.) + H_2\,(g) \rightarrow C_6H_{14}\,(liq.)$,

$\Delta H = -\,30\cdot1 \pm 0\cdot4$ kcal/mole. This figure is in good agreement with the heat of hydrogenation in the gaseous phase as calculated from the difference between the heats of formation of hexane ($\Delta Hf°, g = -\,39\cdot96$ kcal/mole [5]), and of hexene-1 ($\Delta Hf°, g = -\,9\cdot96$ kcal/mole [5]).

TABLE 2.—HEATS OF HYDROGENATION OF FUMARIC AND MALEIC ACIDS

FUMARIC ACID

expt.	wt. acid (g)	H_2 absorbed (cm³ s.t.p.)	$-\Delta H_{\text{obs.}}$ (kcal/mole H_2)
1	0·7192	139·9	25·77
2	0·7238	140·9	25·70
3	0·7283	140·9	25·90
4	0·8075	156·3	25·80
		mean :	25·80 ± 0·07

MALEIC ACID

expt.	wt. acid (g)	H_2 absorbed (cm³ s.t.p.)	$-\Delta H_{\text{obs.}}$ (kcal/mole H_2)
1	0·7269	140·2	31·51
2	0·7192	139·7	31·14
3	0·7277	141·6	31·17
4	0·7385	143·3	31·23
		mean :	31·26 ± 0·15

FUMARIC AND MALEIC ACIDS

The reductions of both these acids were carried out using reduced PdO as catalyst in 15 ml clinical ethanol solvent. Reaction times of *ca.* 20 min were required for complete reduction : uptake of hydrogen was generally a little in excess (by *ca.* ½ %) of theoretical.

The values $\Delta H_{\text{obs.}}$ given in table 2 refer to the formation of succinic acid dissolved in ethanol solution. The heat of solution of crystalline succinic acid in ethanol was measured separately in the "shaking" calorimeter, $\Delta H_{\text{soln.}} = 5{\cdot}35 \pm 0{\cdot}1$ kcal/mole.

From the results in table 2, and the heat of solution of succinic acid, we obtain $\Delta H = - 31{\cdot}15 \pm 0{\cdot}3$ kcal/mole for the heat of hydrogenation of crystalline fumaric acid to form succinic acid, and $\Delta H = - 36{\cdot}61 \pm 0{\cdot}4$ for the corresponding heat of hydrogenation of crystalline maleic acid.

The heats of combustion of crystalline maleic, fumaric, and succinic acids have been measured by Huffman and Fox,[6] whose data lead to the values $-188{\cdot}65 \pm 0{\cdot}09$, $- 194{\cdot}08 \pm 0{\cdot}09$, and $- 224{\cdot}86 \pm 0{\cdot}08$ kcal/mole respectively for the heats of formation. From these, the heats of hydrogenation may be calculated, viz. fumaric acid → succinic acid, $\Delta H = - 30{\cdot}78$, and maleic acid → succinic acid, $\Delta H = - 36{\cdot}21$ kcal/mole; the heat of isomerization of fumaric acid into maleic acid is therefore 5·43 kcal/mole.

The agreement between our directly measured heats of hydrogenation, and those calculated from Huffman and Fox is not exact, but lies within the combined error limits of the two sets of experiments. The agreement between ourselves and Huffman and Fox on the heat of isomerization of fumaric acid is very close, 5·46 against 5·43 kcal/mole.

DODECA-3 : 9-DIYNE

The experiments were made in acetic acid solvent, both Pt and Pd catalysts being used. The hydrogen uptake with Pd as catalyst was generally within ± ½ % of the theoretical, but with Pt catalyst the hydrogen uptake exceeded the theoretical by *ca.* 3 %. The reduction experiments took place readily, reaction times for complete reduction being normally less than 20 min. The $\Delta H_{\text{obs.}}$ values given in table 3 refer to the formation of dodecane in acetic acid solution. The heat of solution of dodecane was measured separately, $\Delta H_{\text{soln.}} = 2{\cdot}25 \pm 0{\cdot}15$ kcal/mole.

DODECA-5 : 7-DIYNE

The experimental conditions were the same as those used in studies on the 3 : 9-isomer. Hydrogen uptake with this compound, however, tended to be slightly less than the theoretical. This may have been due to some decomposition of the diyne, which takes on a yellow coloration on standing.

TABLE 3.—HEATS OF HYDROGENATION OF DIACETYLENES

compound	expt.	wt. diyne (g)	H_2 absorbed		$-\Delta H_{\text{obs.}}$ kcal/mole H_2
			cm³ s.t.p.	% uptake	
dodeca-3 : 9-diyne	1	0·3536	195·2	99·85	128·9
	2	0·5374	295·8	99·56	128·9
	3	0·6020	333·6	100·24	129·1
	4	0·5048	279·1	100·0	128·6
	5	0·4451	244·6	99·4	128·9
	6	0·5810	320·0	99·63	128·9
				mean:	128·9 ± 0·15
dodeca-5 : 7-diyne	1	0·5334	294·4	99·83	125·0
	2	0·3912	213·7	98·8	125·4 *
	3	0·4710	258·2	99·16	125·2
	4	0·4947	270·0	98·7	124·6
	5	0·7888	431·6	99·0	125·0
				mean:	125·0 ± 0·28
octa-1 : 7-diyne	1	0·3912	320·1	96·82	137·1
	2	0·4200	344·5	97·06	138·5
	3	0·4428	363·6	97·18	138·7
	4	0·3640	301·5	98·02	138·1
	5	0·3144	258·9	97·44	138·6
				mean:	138·2 ± 0·58

* Pt catalyst

OCTA-1 : 7-DIYNE

The experiments made use of 0·1 g reduced PdO catalyst, in 10 ml glacial acetic acid solvent. The hydrogen uptake was from 2-3 % low in these experiments, and we presume our sample of diyne was impure. It is suspected that the impurity was xylene, used in washing the sodium during the preparation of the compound. A sample of our preparation was analysed in the micro-analytical laboratory, and corresponded exactly with the formula C_8H_{10}. The values of $\Delta H_{\text{obs.}}$ given in table 3 refer to the formation of octane in acetic acid solution. This heat of solution correction was measured separately, $\Delta H_{\text{soln.}} = 1{\cdot}5 \pm 0{\cdot}1$ kcal/mole.

DISCUSSION

From the results given in table 3, and the heats of solution of the reduction products in acetic acid, we obtain the following heats of hydrogenation:

(i) dodeca-3 : 9-diyne (*liq.*) → dodecane (*liq.*) $\Delta H = -\ 131{\cdot}15 \pm 0{\cdot}5$ kcal/mole,
(ii) dodeca-5 : 7-diyne (*liq.*) → dodecane (*liq.*) $\Delta H = -\ 127{\cdot}25 \pm 0{\cdot}7$ kcal/mole,
(iii) octa-1 : 7-diyne (*liq.*) → octane (*liq.*) $\Delta H = -\ 139{\cdot}7 \pm 1{\cdot}2$ kcal/mole.

These values may be compared with the heats of hydrogenation in the *gas* phase of mono-acetylenes,[7] viz.,

HC≡CH 74·43 kcal/mole
Me . C≡CH 69·14 ,,
Et . C≡CH 69·63 ,,
PrC≡CH 69·50 ,,
BuC≡CH 69·51 ,,

Me . C≡C . Me 65·12 kcal/mole
Et . C≡C . Me 65·80 kcal/mole.

The heat of hydrogenation of EtC≡CEt is not available, but is unlikely to differ from that of EtC≡CMe by more than a few tenths of a kilocalorie per mole. Hence, we see that the heat of hydrogenation of octa-1 : 7-diyne is close to the heat of hydrogenation of *two* moles of 1-butyne (139·26 kcal/mole), and that of dodeca-3 : 9-diyne is close to the heat of hydrogenation of *two* moles of 3-hexyne (*ca.* 131·6 kcal/mole). In both octa-1 : 7-diyne and dodeca-3 : 9-diyne, the —C≡C— groups are separated from one another by a chain of four $—CH_2—$ groups, so that there is little reason to expect any interaction, or conjugation, between them.

In dodeca-5 : 7-diyne, in which the —C≡C— groups are adjacent to each other, the molecule is stabilized by the π-electron conjugation energy of the —C≡C—C≡C— system, and the smaller heat of hydrogenation of the -5 : 7- relative to the -3 : 9- isomer measures the increased energy content of the conjugated diyne. The difference of 3·9 kcal/mole between the heats of hydrogenation of the two isomers is not, however, a direct measure of the overall conjugation energy of the —C≡C—C≡C— system, since the stability of both isomers is unequally influenced by the hyperconjugation effect of the alkyl groups adjacent to the —C≡C— bonds.

Mulliken, Rieke, and Brown [8] have given a formula which enables conjugation energies to be empirically determined from experimentally observed heats of combustion. The empirical hyperconjugation energies obtained in this way are *ca.* 3·5 kcal/mole in alkyl acetylenes, RC≡CH, and from 6-6·5 kcal/mole in dialkyl acetylenes, RC≡CR. Theoretical calculations by Mulliken, Rieke and Brown, and others,[9, 10] indicate that the hyperconjugation energy in R—C≡C—R is twice that in R—C≡CH. Hence, in dodeca-3 : 9-diyne (which we might represent as R—C≡C—R′—C≡C—R) the interaction of the two —C≡C— bonds with the R and R′ groups should result in a net stabilization from hyperconjugation of from 12-13 kcal/mole. In the -5 : 7- isomer (which we might represent by R—C≡C—C≡C—R) the hyperconjugation of the R groups with —C≡C— should give an enhancement only one half of that in the 3 : 9-diyne, i.e. *ca.* 6-6·5 kcal/mole. Thus the overall conjugation energy Δ, of the —C≡C—C≡C— system in the 5 : 7-diyne would need to be of the order 10 kcal/mole to account for our observed difference in the heats of hydrogenation.

Theoretical calculations of the conjugation energy in diacetylene have been made by Mulliken, Rieke and Brown [8] (18·6 kcal/mole), and also by Roberts and Skinner [9] (13·1 kcal/mole). The calculations are sensitive to the choice of values for the unknown parameters involved. More recently, Coulson and Crawford [10] have described an improved method of calculation of conjugation and hyperconjugation energies which is less open to criticism than earlier methods, and we have therefore recalculated the conjugation energy in diacetylene by use of the later method. The internuclear distances in C≡C—C≡C were taken as 1·20 Å (C≡C) and 1·37 Å (C—C), leading to

$$R_x = R_y = 0{\cdot}114\,\beta_0 : \; R = R_x + R_y = 0{\cdot}228\,\beta_0 \equiv 16{\cdot}9 \text{ kcal/mole}$$

($\beta_0 = -$ 74 kcal/mole). To obtain the net conjugation energy Δ from R, the compression energy C of the central C—C bond must be deducted. The required compression energy is that for a C—C, *sp*—*sp*, bond from its normal length to 1·37 Å. Mulliken, Rieke and Brown [8] consider the " normal " length of diagonally bonded C—C to be 0·06 Å less than that of tetrahedrally bonded C—C, in which case the contraction is 1·54 – 0·06 – 1·37 = 0·11 Å. Values of compression energies at different distances are given by Coulson and Crawford,[10] and for $\Delta r = 0{\cdot}11$ Å, $C \sim 5$ kcal/mole, leading to $\Delta = R - C \sim 12$ kcal/mole. The compression energy deduction, however, is difficult to assess precisely, and the calculated Δ value should be accepted with reserve. The agreement between the calculated and empirical Δ values is satisfactory, bearing in mind the assumptions made in estimating both the empirical and calculated values of Δ.

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