[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Single Bond Energies. I. The C–C Bond in Hexaphenylethane[1]

BY HENRY E. BENT, G. R. CUTHBERTSON, MAURICE DORFMAN AND R. E. LEARY

The concept of single–bond energies occupies a position in thermochemistry analogous to that of atomic weights in stoichiometry. In both cases we have conservation laws (conservation of energy and of mass) which make such concepts possible although not necessary. In the field of thermochemistry it has not been established that a definite energy value can be assigned to the bond between two given atoms, which will be independent of the nature of the molecule in which these atoms are found. On the contrary, we know that we cannot calculate the energy of a molecule as the sum of such single–bond energies except as a first approximation and in many cases this is not even a good first approximation. The questions which should be answered are whether we can calculate the energy of a molecule as the sum of constant bond energies plus quantities characteristic of the molecule as a whole determined by steric factors, resonance, etc., or whether we must give up the idea of single–bond energies except as convenient values which enable us to guess at the probable strength of a given bond in certain restricted groups of compounds.

As a first step toward answering these questions we are determining experimentally the magnitude of some of these energies which are characteristic of a molecule as a whole. It is our hope that when these have been evaluated it will be possible to state whether or not the rest of the energy may be accounted for by constant single–bond energies.

In this paper we are reporting work on the C–C bond in hexaphenylethane. This compound has been chosen because there are probably two factors of importance, the steric hindrance in the molecule of ethane and the resonance energy in the free radical molecule, and because these are so large in magnitude as to make their measurement relatively easy. Furthermore, the apparent strength of the C–C bond, or heat of dissociation, has been determined experimentally by Ziegler.[2] The relative importance of steric hindrance and resonance has recently been discussed[3] but the thermal data are not sufficiently accurate to give the desired accuracy in a quantity which is the difference between two very large values.

Hexaphenylethane combines with oxygen readily to form a peroxide. This reaction offers the opportunity of determining the magnitude of the steric effect. If the C–C bond were normal, that is, had the strength of a C–C bond in a simple hydrocarbon, then we would expect the heat liberated by the oxidation to be that due to the formation of two C–O single bonds less the value for the C–C bond and the energy of converting the O=O bond into the O–O bond. We are here using the concept of constant single–bond energies in our calculation of the inconstancy of the C–C bond in hexaphenylethane. This apparent inconsistency is justified by the fact that single–bond energies are good first approximations in the type of compound to which we have applied them and the effect of steric hindrance we expect to be much larger than any inaccuracy due to these assumptions. Any energy liberated in the reaction of oxidation in excess of that calculated by this method we attribute to the weakening of the bond in hexaphenylethane due to steric hindrance.

We know the combined influence of steric hindrance and resonance which is the difference between the value for a normal bond and the heat of dissociation as determined by Ziegler. Thus we are able to calculate also from our measurements the magnitude of the resonance energy of triphenylmethyl.

Experimental Procedure

In making a run the capsule is first charged with the compound to be studied, the capsule sealed off and weighed, to give the weight of the sample. With hexaphenylethane this charging is all done in an inert atmosphere.[4] The capsule is then placed in the apparatus as described under J, Fig. 1. The Dewar flask is half filled with benzene and the desired quantity of catalyst added if the experiment is to be a hydrogenation. The Dewar is placed in position and held by rubber bands (not shown) at the ground joint. Repeated evacuation and filling with gas removes all air. Gas is then introduced and shaking continued until the benzene has become saturated and the temperature has become steady. The temperature is determined by means of the thermocouple and a L and N type K potentiometer. When the temperature has become steady for a

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[1] This work has been possible in part by reason of a grant from the Milton Fund of Harvard University.

[2] Ziegler and Ewald, *Ann.*, **473**, 163 (1929).

[3] Bent and Ebers, THIS JOURNAL, **57**, 1242 (1935).

[4] Dorfman, *ibid.*, **57**, 1455 (1935).

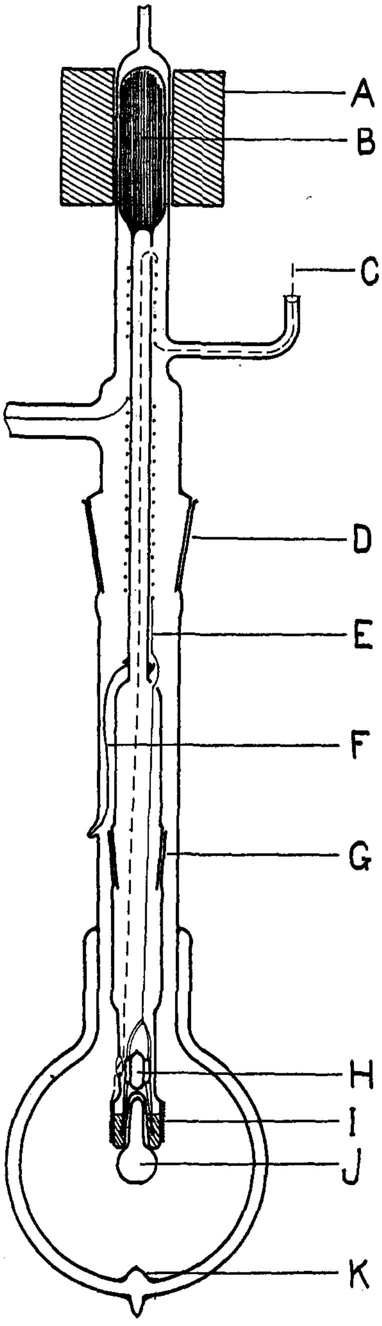

Fig. 1.—A is an electromagnet which is used only at the beginning of each run to raise the unit holding the capsule. When the current is turned off this unit drops and breaks the capsule on the bottom of the Dewar. B is a bundle of soft iron wire which is lifted by the electromagnet. C represents the heater lead. This consisted of four strands of No. 22 lacquered copper wire. The wires were connected in pairs, four wires being used in order to cut down lead resistance. The double wire may also be used in calibrating the heater. The heater lead passes up around the glass tube in a spiral and finally enters at a hole at the top, coming out through a second hole at the bottom where it is attached to the heater. D is a standard 20 mm. ground joint necessary for charging the apparatus for a run. E represents the twenty wires of the ten-junction thermocouple. These wires pass through a hole just below E and from there down are within the glass tube. Above E these wires pass around the glass tube in a spiral to give flexibility and finally pass out through a tube at the left just below C. F is a heavy copper wire which keeps the glass tube and capsule from resting on the bottom of the flask before the beginning of a run. The lower end of this wire rests in a small recess in the outer glass tube. The upper end hooks into an eye in a ring passing around the glass tube just below E. When the current is passed through the electromagnet the center unit is raised, the copper wire falls away from its recess and when the current is turned off the tube holding the capsule is free to drop to the bottom of the Dewar. G is a ground joint to permit introducing the junctions of the thermocouple in a symmetrical manner in the bottom of the tube. This joint was lubricated with "Stacol" which is a glass insoluble in organic solvents produced by Glyco Products Co. This glass softens a little below 100°. Essentially this gives a glass seal which can still be broken easily in case repairs become necessary. H is a very small glass cylinder which supports the ten junctions of the thermocouple during the construction of the apparatus. It is sealed at both ends. Ten glass rods, about the diameter of the two thermocouple wires and the length of the cylinder are sealed around this cylinder in such a way as to form ten longitudinal recesses for the wires. After placing the wires in position they were held firmly in place by wrapping with fine silk thread. I is the heater made from No. 25 nichrome wire and having a resistance of 4.37 ohms. These wires were held in place by a little insolute cement. Just inside of the heater and separated from it by the glass tube are located the junctions of the thermocouple. These are imbedded in a little paraffin which is indicated by the cross hatching. J is the capsule containing the compound whose heat of reaction or solution is to be determined. The neck of this capsule is held in a small recess which goes up between the junctions of the thermocouple. By choosing the proper size tube for the construction of the capsule it is possible to hold it in this position by winding the proper amount, a few turns, of cotton thread around it. The friction then holds it in position. The bottom of this capsule is blown rather thin and flattened in the flame. This last precaution greatly aids in the breaking of the capsule. K is a point in the bottom of the Dewar flask which strikes and shatters the capsule when the latter is dropped. The severity of the blow which shatters the capsule can be readily controlled by a rheostat which varies the current through the electromagnet. Since the thermocouple leads and the heater leads have considerable spring an increase in the current compresses the coils of these leads and increases the severity of the blow which breaks the capsule. The Dewar is silvered in order to decrease heat loss and protect photosensitive compounds from decomposition.

time sufficient to permit the calculation of the correction for cooling the electromagnet is turned on momentarily, which first raises the capsule and then causes it to smash on the bottom of the Dewar. As the temperature rises the potentiometer readings are taken and at the same time the volume of gas absorbed is measured. This permits one to check the purity of the compound, the nature of the reaction, and if necessary to calculate the heat of the reaction from the quantity of gas absorbed in case the reaction becomes so slow near the end as to make the heat loss through the Dewar a serious correction. This latter procedure has not become necessary as yet although the hydrogenation of heptene required over two hours for substantial completion. At the end of the run the temperature is again recorded for a time interval sufficiently long to permit proper corrections for heat loss. Current is then passed through the heater at the rate of about 0.5 amp. (one watt) for an interval of time sufficient approximately to duplicate the rise in temperature produced by the reaction and again the rate of cooling determined after the electrical heating. This electrical calibration of the apparatus after each run makes it unnecessary to determine the heat capacity of the apparatus or control the amount of solvent. As will be described below, we also checked the apparatus by determining the heat of hydrogenation of heptene. During the time of electrical heating the thermocouple measurements were not significant, being approximately one degree higher than the temperature of the benzene due to the small distance from the hot junctions to the heater. Equilibrium was established very quickly after the heating and consequently there was no trouble in calculating the rise in temperature. At the completion of a run the product of the reaction was recovered and identified.

Experimental Error

A precision of about 1% seems to be attained rather readily by the method described above although any considerable increase in accuracy would involve a tremendously greater expenditure of effort and much more expensive apparatus. Some of the numerous errors will be briefly discussed. The temperature rise was usually from one to two degrees centigrade. The potential could be read to about one microvolt (0.0025°) but it is doubtful if the determination is better than 0.005° on account of stray thermal e. m. f.'s in the potentiometer. The heat lost through the Dewar is small for the oxidations and the electrical calibration, being of the order of 1% of the total heat involved. However, in the case of the hydrogenation, which was much slower, this heat amounted to more than 10% of the total. This quantity is probably not determined with a precision of much better than 10% for reasons given below. The electrical energy was not determined with a precision of much more than 1% although this measurement could be improved without much difficulty if it seemed desirable to do so. Most important of all, however, we have no evidence that our hexaphenylethane is much better than 99% pure. This compound is not easy to prepare in a high state of purity nor is there any method known for establishing the purity of a sample with any higher precision than this. Furthermore we cannot be sure that the reaction in

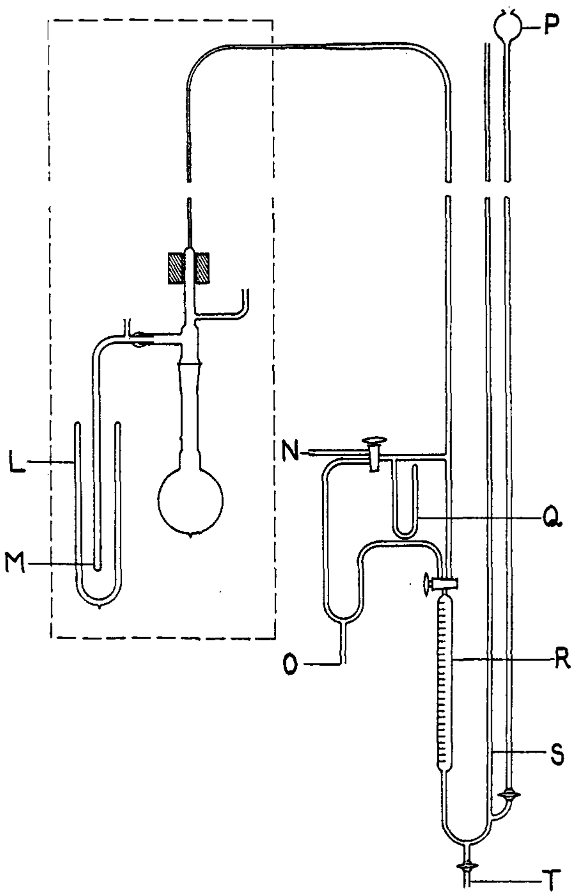

Fig. 2.—L is a Dewar which contains the cold junction of the thermocouple and is kept at the ice point. M is a glass tube containing the cold junctions. All of the apparatus enclosed by the dotted line is mounted on a shaker which provides the necessary agitation of the solution. This shaker can be controlled for amplitude and frequency and can be operated to produce vigorous swirling of the solution without breaking the glass lead [Bent, *Ind. Eng. Chem., Anal. Ed.*, **2**, 106 (1930)]. The lead for oxygen or hydrogen is several meters long and provides ample flexibility. N leads to the pump, for evacuation at the beginning of a run, the solvent vapor serving to sweep out all air. O leads to the source of oxygen or hydrogen. P is a mercury reservoir which supplies the necessary control of pressure. It is possible to carry out a hydrogenation at about three atmospheres pressure if necessary. Q is a small mercury manometer useful in testing for leaks and checking the progress of the preliminary evacuation. R is a buret which measures the volume of gas absorbed by the reaction. S is a tube open to the atmosphere which permits one to read the pressure in the buret on a scale (not shown). T is a stopcock for removing mercury from the buret when this is to be refilled from the gas supply. The mercury removed from T is poured back into P for future use.

which we are interested has no side reactions which may not amount to as much as 1%. It would probably be possible to clear up some of these questions if there seemed to be any adequate reason for obtaining a more precise result but for the purposes of this investigation 1% is quite sufficient to establish the importance of the factors which we are studying. A further reason for finding little use at the present time for highly precise values for reactions carried on in solution arises from the fact that a considerable fraction of the total energy may result from the nature of the solvent in which the reaction is conducted. Since the solvent frequently alters the heat of a reaction by as much as 1–2 kcal. it is doubtful if values determined with any greater precision than this have significance in predicting reactions in solution at the present time. In the case of the oxidation of hexaphenylethane the problem is further complicated by the fact that the peroxide formed in the reaction is only slightly soluble and does not readily come to equilibrium with the saturated solution. It is thus probable that some uncertainty in the cooling correction at the end of a run is due to the fact that the solution becomes supersaturated with the peroxide and the erratic way in which this material crystallizes.

Material

Hexaphenylethane.—Eastman c. p. triphenylcarbinol was first recrystallized from 95% ethyl alcohol and then converted into triphenylchloromethane by the method of Halford.[5] The benzene solution of the chloride was dried with calcium chloride overnight to ensure complete reaction. The conversion of the chloride into hexaphenylethane was accomplished by lead amalgam as described by Gomberg,[6] using an inert atmosphere and an all-glass closed system as described by Dorfman.[4]

The hexaphenylethane was recrystallized from acetone and then washed with the same solvent, the whole procedure being carried out in a closed system. The yield of product was a little more than half the weight of the original chloride. The purity was established by determining the volume of oxygen absorbed during the course of a heat measurement. This volume was corrected for the change in the vapor pressure of the benzene as a result of the heat liberated in the oxidation and was found to be within 0.5% of the calculated amount of oxygen. This is as accurate as the correction for the vapor pressure of the benzene could be made. Another check on the purity of the sample was to measure the amount of hydrogen which a sample would absorb with platinum as a catalyst. This also indicated less than 1% impurity. The product of this reaction was identified, by a mixed melting point, as triphenylmethane.

The hydrogen was supplied by the Ohio Chemical Co. especially for hydrogenation. The oxygen was supplied by the Air Reduction Co. The benzene was Merck Grade 1, thiophene-free reagent.

Experimental Results

To establish the reliability of the experimental procedure it seemed desirable to check a known reaction. For this purpose heptene-1 was chosen. We are greatly indebted to Professor Kistiakowsky and co-workers for a sample of their heptene-1 and for the use of a quartz spiral gage which was used in determining the vapor pressure curve for this compound.

The values obtained for ΔH for the hydrogenation of heptene are -28.7 and -29.1 kcal. per mole. The heat corresponds to the conversion of one mole of heptene in dilute solution at 25° to one mole of heptane in dilute solution with benzene as the solvent. These values were obtained by basing the calculation on the lowest temperature reached just after the capsule was broken. From this initial drop in temperature the value of ΔH for the reaction heptene (liquid) $\longrightarrow$ heptene (soln.) was found to be $+0.6$ and $+0.4$. Combining these values gives for the reaction of liquid heptene to give heptane in solution -28.1 and -28.7, or a mean value of -28.4. The heat of solution of heptane in benzene is given in the "I. C. T." as $+1.05$. We measured this quantity, using heptane supplied by Eastman Kodak Co., and obtained values of $+1.24$ and $+1.28$. Since our apparatus is not designed for the determination of such a small quantity we chose the value of 1.1 to combine with the above data to give for the heat of hydrogenation of liquid heptene to give liquid heptane the value of -29.5. In order to compare our value with that of Kistiakowsky and co-workers it is necessary to determine the value for the reaction in the vapor state. The heat of vaporization of heptane is given in "I. C. T." as 7.6 kcal. We have determined the vapor pressure of heptene from about 0 to 90° and from these data have calculated the heat of vaporization. These results are given in Table I. Combining the value so obtained of 8.1 ± 0.1 kcal. gives for the reaction gaseous heptene at 25° plus hydrogen to give gaseous heptane at 25° a value of ΔH of -30.0 kcal. The value obtained by Kistiakowsky and co-workers[7] for this reaction is -30.141 ± 0.037 kcal. at 82°. Assuming the value for ΔC_p to be the

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[5] Halford, This Journal, **53**, 105 (1931).

[6] Gomberg and Schoepfle, *ibid.*, **39**, 1652 (1917).

[7] Private communication, *ibid.*, **58**, 137 (1936).

same as for the ethylene reaction[8] we obtain from their data a value at 25° of 29.91. This is an excellent agreement and well within our experimental error. This agreement is remarkably good considering the fact that the reaction was rather slow and required more than two hours for completion.

TABLE I

VAPOR PRESSURE OF *n*-HEPTENE-1

T, °K.	Pressure, mm.	*T*, °K.	Pressure, mm.
273.2	17.0	314.9	127.5
273.3	17.3	314.9	127.4
273.3	17.3	336.0	284.3
273.3	17.4	335.8	282.4
294.3	49.7	335.5	279.3
294.3	50.5	335.2	276.6
294.3	50.7	361.9	655.6
294.3	51.0	361.2	643.5
294.4	51.4	350.5	634.0
315.4	129.3	350.1	623.5
315.2	129.0		

The oxidation of hexaphenylethane proceeded much more rapidly and from this standpoint should give much more concordant results. The chief difficulty encountered in these reactions was the insolubility of the peroxide and the tendency of this compound to supersaturate. This introduced two errors. In the first place, in order to express the reaction in terms of a single product it became necessary to determine the heat of solution of the peroxide. It might have seemed simpler to have used such a small amount of material as to produce no precipitate. However, this would have necessitated the use of about 0.1 g., which would have been too small an amount of material to give an accurate value for the heat of oxidation. Again, one might have started with a saturated solution of the peroxide. However, the tendency of the solution to supersaturate in any case would prevent this being a solution of our difficulty. Consequently we carried out runs using about 1.5 g. of hexaphenylethane and then corrected for the amount of material remaining in solution. In two runs this was 0.5 and 0.8 g. in 150 cc. of benzene, although we were not able to dissolve more than 0.1 g. starting with the peroxide. After the completion of a run peroxide continued to crystallize from the solution for many hours. The heat of solution of the peroxide was then determined. The value so obtained ($\Delta H = +8.8 \pm 2.0$ kcal.) is not very precise because the weight of the sample was but 0.1 g. This gives for the heat of oxidation of solid hexaphenylethane to give solid peroxide a value of -45.5 ± 0.5 kcal. Since most of the peroxide crystallized during the heat measurement the uncertainty in the value for the heat of solution of the peroxide does not introduce an equal uncertainty in the heat of the oxidation reaction. We have also determined the heat of solution of hexaphenylethane and obtained the value 2.6 kcal. This figure was obtained by determining the heat of solution of hexaphenylethane and then correcting for the fraction of the material which dissociated in solution. The measured heat was 3.8 kcal. per mole. Using 10^{-4} for the value of the equilibrium constant (expressing concentrations as mole fractions) enables one to calculate that about 11% of the ethane was dissociated in dissolving. Taking Ziegler's value of 11 kcal. for the heat of dissociation of hexaphenylethane gives for the solution of solid hexaphenylethane to give undissociated material in solution a value of 2.6 kcal. With this and the value for the heat of solution of the peroxide of 8.8 ± 2.0 we obtain for the heat of reaction in solution the value -39.3 ± 2.0 kcal. We consider this value in solution to be more nearly comparable to the value in the gas phase on account of the experiments of Conant and Thompson[9] on the effect of solvent on the keto enol equilibrium.

We are now in a position to compare our result with the value to be expected if the bonds involved in these reactions were normal. Using the values for single-bond energies suggested by Pauling[10] we can write the following reactions in which R represents triphenylmethyl and R_2 hexaphenylethane. (The free radical is not to be considered stabilized by resonance.)

		ΔH	
R_2	$\longrightarrow 2R$	$+84$	
O_2	$\longrightarrow 2O$	$+117$	
$2O$	$\longrightarrow O—O$		-35
$2R + O—O$	$\longrightarrow R—O—O—R$		-166
$R_2 + O_2$	$\longrightarrow ROOR$	$+201$	$-201 = 0$

Hence one would expect that there would be zero heat of oxidation. This prediction is based on the assumption of Pauling and Wheland, and of Hückel,[11] that the dissociation of free radicals is due not to the weakness of the bond in the ethane but to the stabilization of the free radical as a result of the resonance energy of the latter. The value -39.3 kcal. which we have obtained for the heat of oxidation indicates that the C–C in the

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(8) Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935).

(9) Conant and Thompson, *ibid.*, **54**, 4039 (1932).

(10) Pauling and Sherman, *J. Chem. Phys.*, **1**, 607 (1933).

(11) Pauling and Wheland, *ibid.*, **1**, 362 (1933). Hückel, *Z. Physik*, **83**, 632 (1933).

ethane is not a normal bond but is somewhat weaker due probably to steric hindrance in the molecule of ethane. Any weakening of this bond in the ethane will appear as a larger amount of heat liberated in the oxidation. Hence we must conclude that the bond has been weakened by about 39.3 kcal. This agrees with the result calculated by Bent and Ebers[3] from thermal data which showed a weakening of the C–C bond of 36 kcal. The agreement between the two results is much better than the accuracy of either of the experimental data. The apparent strength of the C–C bond as determined from the temperature coefficient of the equilibrium constant is found to be 11 kcal.[2] Hence we may conclude that the phenomenon of dissociation of free radicals is due about equally to the weakness of the bond in the ethane and to the stabilizing effect of resonance in the product of dissociation. We cannot be precise in stating the relative importance of steric hindrance and resonance energy on account of uncertainty in the values to be assigned to single-bond energies.

Conclusions

1. A general method has been described for determining heats of reactions. This is particularly suited to the study of easily oxidized substances which must be kept out of contact with the air. This apparatus permits the simultaneous measurement of the amount of gas absorbed or evolved by the reaction.
2. The vapor pressure of *n*-heptene-1 has been determined from 0–90° and from these data the heat of vaporization calculated.
3. The heat of hydrogenation of *n*-heptene-1 and the heat of oxidation of hexaphenylethane, together with the heats of solution of the compounds involved in these reactions have been determined.
4. The dissociation of hexaphenylethane is found to be due about equally to the weakening of the C–C bond in the ethane and to the stabilizing effect of the resonance energy of triphenylmethyl.

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Single Bond Energies. II. The C–C Bond in Hexaphenylethane[1]

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The strength of the C–C bond in hexaphenylethane has been calculated recently from measurements of the heat of oxidation to give the peroxide.[2] The result of this investigation was the assignment of about half of the apparent weakening of the C–C bond, as compared with normal hydrocarbons, to steric hindrance and the other half to the phenomenon of resonance. These conclusions rest upon certain assumptions regarding single bond energies involved in the calculations, especially the oxygen–oxygen single bond and the oxygen–carbon bond.

As an independent method of testing the above conclusions work has been continued and the heat of hydrogenation of hexaphenylethane to give triphenylmethane has been measured. From this result one may proceed as in the case of the oxidation to calculate the relative importance of steric hindrance and resonance energy. The advantage of studying the hydrogenation reaction is not only that a check is obtained on the conclusions from the oxidation but also that the assumptions regarding single bond energies which appear in the calculations are quite different and are probably less open to question. The experimental procedure has been fully described in the first paper of this series. In order to obtain a rate of hydrogenation which was sufficiently high to give accurate determinations of the heat of the reaction it was necessary to use a promoter with the platinum catalyst.[3] Considerable difficulty was encountered when benzene was used as a solvent. When the reaction was sufficiently rapid to be satisfactory the benzene frequently was hydrogenated. One fairly satisfactory run was obtained using benzene as a solvent. Although this checked the results quite well which were obtained using a different solvent it was not used in the

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(1) This work has been made possible in part by reason of a grant from the Milton Fund of Harvard University.

(2) H. E. Bent, G. R. Cuthbertson, Maurice Dorfman and R. E. Leary, THIS JOURNAL, 58, 165 (1936).

(3) Gilman, "Organic Syntheses," Coll. Vol. I, 1932, p. 452.