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.

CAMBRIDGE, MASSACHUSETTTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

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

BY HENRY E. BENT AND G. R. CUTHBERTSON

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.

final calculations. The solvent finally chosen was ethyl acetate. The reaction was complete in about forty-five minutes using 0.75 g. of hexaphenylethane and 0.2 g. of catalyst with 0.003 g. of $FeCl_2{\cdot}4H_2O$ as promoter in 150 cc. of solvent. The volume of hydrogen taken up during a run was within 3% of that calculated from the initial weight of the compound. This 3% may be due entirely to reaction of catalyst with hydrogen. The amount of oxygen absorbed by the hexaphenylethane was within 0.5% of the calculated amount. The product of the reaction, which was contaminated by ferric chloride, melted at 82° and gave with triphenylmethane a mixed melting point of 83°. The sample of triphenylmethane used melted at 84°. This seemed quite satisfactory considering that the product had not been recrystallized after the run.

Experimental Results

All data are reported as values of ΔH.

The average value for the heat of hydrogenation obtained from four runs is -31.1 ± 0.5 kcal. per mole. This is for the addition of one mole of hydrogen to one mole of solid hexaphenylethane to give two moles of triphenylmethane in solution in ethyl acetate. In order to express the results in terms of either solid materials, or the same materials in solution, it was necessary to determine the heat of solution. This was done in the case of triphenylmethane both in the presence and absence of catalyst in order to eliminate the possibility of a heat of adsorption of the product of the reaction on the catalyst. No significant difference in the heat of solution was observed in these two cases. The value of ΔH for the solution of triphenylmethane in ethyl acetate is $+4.7 \pm 0.1$ kcal. The value for the solution of hexaphenylethane was found to be $+5.1 \pm 0.1$ kcal. This must be corrected for the fraction of the ethane which dissociated during the process of solution. The value of the equilibrium constant for this purpose is taken as 10^{-4}, expressing the concentrations as mole fractions, and the value of the heat of dissociation from Ziegler's measurements[4] as 11 kcal. The amount of dissociation is found to be 13% and therefore the value for the heat of solution of hexaphenylethane to give associated material in solution is 3.7 ± 0.1 kcal.

We are now in a position to combine the values of the heat of solution with the experimentally determined heat of hydrogenation. Taking twice the heat of solution of triphenylmethane with the heat of hydrogenation gives for the reaction solid hexaphenylethane plus hydrogen to give solid triphenylmethane a value of -40.5 kcal. Likewise the value for the heat of solution of hexaphenylethane combined with the experimentally determined heat of hydrogenation gives for the reaction hexaphenylethane in solution plus hydrogen to give triphenylmethane in solution a value of -34.8 kcal. As mentioned in the first paper of this series, we believe this latter value to be nearer the value for the reaction in the gas phase than the value involving solids.

These values are quite independent of any peculiar properties of triphenylmethyl. It has frequently been suggested that the existence of free radicals in solution is due largely to an interaction of the free radical with the solvent and that in the gaseous state no such effect would be possible. This criticism, however, does not seem well founded when one considers the large number of solvents investigated by Ziegler and Ewald and the fact that there seemed to be little specific effect of solvent. Ziegler and Ewald report equilibrium constants and values for ΔH of dissociation. This method appears to indicate a large effect of solvent on the equilibrium but very little effect on the heat. If, however, we determine the effect of the solvent on the free energy change for the reaction and on the heat of the reaction, as has been done by Conant,[5] we find about the same effect in both cases, namely, about 1.5 kcal. If the solvent were largely responsible for dissociation one would not expect dissociation to be independent of the nature of the solvent. The values here reported, however, are not expressed in terms of triphenylmethyl and are not related to any possible peculiarities of this compound. The results offer a direct method of calculating the lack of stability of the molecule of hexaphenylethane. The subsequent calculation of the resonance energy of triphenylmethyl as the difference between the value which we find for steric hindrance and the experimental value of ΔH of dissociation is, of course, dependent upon the assumption that interaction of triphenylmethyl with solvent is not very significant.

Discussion of Results

The value which we find for ΔH for the reaction of addition of hydrogen to hexaphenylethane in

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(4) Ziegler and Ewald, *Ann.*, **473**, 163 (1929).

(5) Conant, *J. Chem. Phys.*, **1**, 427 (1933).

solution to give triphenylmethane in solution (-34.8 ± 0.5 kcal.) is now to be compared with the value predicted from single bond energies. We may write a series of equations, similar to those which we used in the first paper of this series in calculating the value for the oxidation of hexaphenylethane, using Pauling's values for single bond energies.

$$\begin{array}{rcll} & & & \Delta H \\ R_2 & = & 2R & +84 \text{ kcal.} \\ H_2 & = & 2H & +102.4 \\ 2R + 2H & = & 2RH & -199.4 \\ \hline R_2 + H_2 & = & 2RH & -13 \text{ kcal.} \end{array}$$

This calculated value is considerably different from the experimental value of -35 kcal. The difference is to be attributed to a weakening of the carbon-carbon bond in hexaphenylethane to the extent of 22 kcal. The value found for this weakening, however, from our measurements on the heat of oxidation was 39 kcal. While both results agree in indicating a rather large steric effect the agreement is far from satisfactory and cannot be attributed to experimental error. Evidently the values which have been chosen for the single bond energies are not in accord with these experimental measurements. Subsequent to the assignment of single bond energies by Pauling, considerable experimental data have appeared which make necessary a reassignment more in accord with these recent results. Rossini[6] gives the heat of combustion of normal hydrocarbons containing more than five carbon atoms as $60.40 + 157\,n$, in which n represents the number of carbon atoms. We can, therefore, calculate the heat of the reaction

$$C_nH_{2n+2} + H_2 = 2C_{n/2}H_{n/2+2}$$

from the above formula and the heat of combustion of hydrogen to give water, 68.313. The value of ΔH so calculated for the above reaction is -7.91 kcal. This is the value for the addition of hydrogen to a single bond in a normal hydrocarbon to give two molecules each with half the number of carbon atoms. As this is an experimentally determined quantity it is much to be preferred over the value of -13 kcal. calculated above. Calling this in round numbers 8 kcal. gives, when combined with the experimental value for the heat of hydrogenation, a value for the effect of steric hindrance of 27 kcal.

In a similar manner we may now consider the value calculated for the oxidation of hexaphenylethane from single bond energies. This may be obtained from single bond energies according to the equations

$$\begin{array}{rcll} & & & \Delta H \\ R_2 & = & 2R & +84 \text{ kcal.} \\ O_2 & = & 2O & +117 \\ 2O & = & O\text{-}O & -35 \\ 2R + O\text{-}O & = & ROOR & -166 \\ \hline R_2 + O_2 & = & ROOR & 0 \end{array}$$

We may also obtain a value for the heat of oxidation without using so many single bond energies. In the following equations, (a) is obtained from Rossini's values for heats of combustion as indicated above; (b) is obtained from Rossini's values using the heat of oxidation of alcohols; (c) and (d) can be obtained only by making certain assumptions as to the constancy of single bond energies. We assume that an O-H bond in an alcohol is the same as that in water. The heat of formation of water vapor (58.6) combined with half the dissociation of oxygen (58.5) gives for the removal of hydrogen forming an oxygen atom the value of 117.1.

$$\begin{array}{rcll} & & & \Delta H \\ H_2O & = & H_2 + {}^1/_2O_2 & 58.6 \text{ kcal.} \\ {}^1/_2O_2 & = & \text{-}O\text{-} & 58.5 \\ \hline H_2O & = & H_2 + \text{-}O\text{-} & 117.1 \end{array}$$

The last value (d) is that chosen by Pauling for the single bond between oxygen atoms in peroxides. For convenience we will let R represent a hydrocarbon chain of more than five carbon atoms, less a terminal hydrogen.

$$\begin{array}{rclll} & & & \Delta H & \\ R_2 + H_2 & = & 2RH & -8 \text{ kcal.} & \text{(a)} \\ 2RH + O_2 & = & 2ROH & -78 & \text{(b)} \\ 2ROH & = & 2RO\text{-} + H_2 & +117.1 & \text{(c)} \\ 2RO\text{-} & = & ROOR & -35 & \text{(d)} \\ \hline R_2 + O_2 & = & ROOR & -4 & \end{array}$$

This series of equations differs from the last set, which gives a value for the same reaction, in that we have substituted for the bonds (C-C, O=O and C-O) two experimental quantities and the assumption an O-H bond is the same strength in an alcohol and in water. This last method seems to involve fewer arbitrary assumptions and therefore in view of the fact that our heat measurements also indicate that the second method is to be chosen we accept this value of -4 kcal. From this we calculate for the weakening of the C-C bond in hexaphenylethane from the heat of oxidation a value of 35 kcal.

We may now summarize the various ways in which we have calculated the weakening of the C-C bond in hexaphenylethane. These are four in number. First, we have compared the value for the heat of combustion with that predicted by

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(6) Rossini, *Bur. Standards J. Research*, **13**, 21, 189 (1934).

the empirical equations of Kharasch.[7] This gave a weakening, which we attribute to steric hindrance, of 36 kcal. The second method, discussed in the same reference, is to compare the heat of combustion of hexaphenylethane with that of triphenylmethyl. This also gave a value of 36 kcal. Both of these estimates seemed rather unreliable due to the very large values of the heats of combustion. The value obtained from the heat of oxidation to give the peroxide is 35 kcal. and the value from the heat of hydrogenation, which should from theoretical considerations be the best value, is 27 kcal. The disagreement between these last two values is not necessarily experimental error as the reactions were carried out in different solvents, and involve the heats of solutions of the reactants and products of the two reactions. Until we have data on the heats of vaporization it will not be possible to compare the reactions in the gaseous phase. We may conclude, therefore, that the carbon–carbon bond in hexaphenylethane is weaker than a normal bond by about 30 kcal. This is about half of the total effect giving rise to free radicals, the remainder presumably being that of resonance in the free radical as discussed by Pauling and Wheland.[8]

Summary

1. The heat of hydrogenation of hexaphenylethane to form triphenylmethyl has been measured. The values obtained are −40.5 when the reaction involves solids and −34.8 when the reaction involves materials in solution in ethyl acetate.

2. The carbon–carbon bond in hexaphenylethane is calculated to be weaker than a normal bond by about 30 kcal.

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

[8] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

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[CONTRIBUTION FROM THE RANDAL MORGAN LABORATORY OF PHYSICS, UNIVERSITY OF PENNSYLVANIA]

The Structure of Thin Films of Metallic Oxides and Hydrates

BY NEWBERN SMITH

Iron is known to form a number of different oxides and hydrates, which differ chemically as well as physically. Oxide films have been removed from the surfaces of heated and passive iron by U. R. Evans,[1] using both chemical and electrolytic corrosion. He stated that the films consist for the most part of non-magnetic ferric oxide, but left unsettled the question of their contamination with hydroxides or other oxides of iron. It is possible that such contamination, as well as any pseudomorphism or peculiarities of structure of the films, of the kind suggested by Tammann,[2] may well affect the corrosion of the metal.

Save for Thomson's original article,[3] a few experiments of Boas and Rupp on passive iron,[4] and an investigation of the corrosion of iron by J. Cates,[5] no electron diffraction studies of iron oxide or hydroxide films have been reported in the literature.

The primary object of this research was to investigate by electron diffraction the nature and structure of the oxide film which forms on iron on warming in air, and to correlate the results with data obtained from studies of films formed on other metals and on the surfaces of solutions of metallic salts.

Experimental

Apparatus.—The electron diffraction camera used has been described in another article.[6] Thirty to fifty kilovolts were used in obtaining the diffraction patterns. A gold foil pattern was photographed, as a standard of comparison, for every pattern obtained from an unknown substance. Each film to be investigated was mounted on a specimen holder consisting of a thin brass disk pierced by 0.1-mm. holes. This hole served as the final collimating hole for the electron beam.

Preparation of Specimens.—A thin strip of the metal whose oxide film was to be removed was made the anode in an electrolytic cell consisting of three petrie dishes connected by strips of absorbent cotton. The electrodes and electrolyte were placed in the end dishes, while the middle dish was filled with a solution of the metallic chloride or sulfate, in order to hinder the migration of the cathodically produced hydroxyl ions. A current density of about 10 m. a. per sq. cm. was sufficient to undermine the film, which was then loosened by a much larger current. The isolated film was prepared for mounting by washing in several changes of water.

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[1] Evans, *J. Chem. Soc.*, 1020 (1927); 2651 (1929).

[2] Tammann, *Stahl und Eisen*, **42**, 617 (1922).

[3] Thomson, *Proc. Roy. Soc.* (London) **128**, 649 (1930).

[4] Boas and Rupp, *Ann. Physik*, **13**, 1 (1932).

[5] Cates, *Trans. Faraday Soc.*, **29**, 817 (1933).

[6] Morgan and Smith, *Rev. Sci. Inst.*, **6**, 316 (1935).