[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

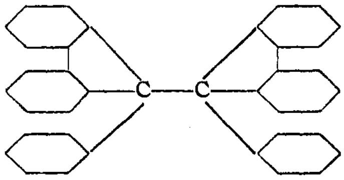
Single Bond Energies. III. The C–C Bond in Diphenyl Di-biphenylene Ethane

BY H. E. BENT AND J. E. CLINE

The first two papers of this series give an answer to a question regarding the strength of the C–C bond in hexaphenylethane.[1] Until the approach to the problem with the aid of wave mechanics it had been assumed that the C–C bond is weak in those ethanes which dissociate to give free radicals. Quite the opposite point of view has been suggested by Pauling and Wheland[2a] and by Hückel.[2b] These authors assume that the C–C bond is normal and that dissociation is caused by a stabilization of the free radical as a result of the resonance energy made possible by the presence of an odd electron and the unsaturated structures in the benzene rings. The evidence presented from a study of the heat of oxidation and the heat of hydrogenation of hexaphenylethane leads to the conclusion that neither point of view is entirely correct but that about half of the "*apparent*" weakening of the C–C bond is due to a weakening of the bond in the ethane. We have assumed that this bond is weaker than normal on account of steric hindrance.

Many problems are suggested by these experiments. The one with which we wish to deal in this paper is the question as to what extent variation in the degree of dissociation of various ethanes is due to differences in steric hindrance in the ethane and to what extent due to different amounts of resonance energy in the various free radicals.

Diphenyl di-biphenylene ethane is chosen for this study on account of its remarkable properties.



Although very closely related to hexaphenylethane it exhibits a very different behavior. The loss of four hydrogens and tying together of the benzene rings produces an ethane which dissociates much less than hexaphenylethane. Pauling and Wheland have accounted for this decreased dissociation by a smaller amount of resonance energy in the free radical. Conant[3] has pointed out the striking difference between the properties of phenyl xanthyl and phenyl fluoryl. In one case the benzene rings are tied together by means of oxygen and in the other case are tied together directly. Yet phenyl xanthyl is less associated than triphenylmethyl and phenyl fluoryl is more associated. If one constructs models for these free radicals it becomes apparent that steric hindrance might be much less in the case of phenyl fluoryl. We therefore wished to compare experimentally the strength of the C–C bond in diphenyl di-biphenylene ethane with the bond in hexaphenylethane. In the first two papers of this series we evaluated the strength of the C–C bond by making use of Pauling's single bond energies. For the purpose of the comparison which we now propose to make it is not necessary to know any values for single bond energies. We may interpret our experimental results with the aid of the assumption that the strength of the C–O and O–O bonds in the various peroxides formed is the same.

Another reason for studying the heat of oxygenation of this particular compound arose in connection with the determination of the free energy of addition of sodium to diphenyl di-biphenylene ethane. These experiments indicated that the free energy of addition of sodium to phenyl fluoryl is more negative than in the case of triphenylmethyl by about 12 kcal.[4] This was a very unexpected result since Wheland has suggested from theoretical considerations that the electron affinity as a first approximation should be a constant for organic free radicals. His conclusion is quite in accord with experimental investigations of these compounds.[5] If the resonance energy of phenyl fluoryl is large, then steric hindrance must be very small in order to give a compound which is only very slightly dissociated. A small steric effect should lead to a stronger C–C bond and hence a much lower heat of oxidation.

Experimental

The apparatus has been considerably improved and changed in a number of important respects since the work

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[1] Bent, Cuthbertson, Dorfman and Leary, THIS JOURNAL, **58**, 165 (1936); Bent and Cuthbertson, *ibid.*, **58**, 170 (1936).

[2] (a) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933); (b) Hückel, *Z. Physik*, **83**, 632 (1933).

[3] Conant, *J. Chem. Phys.*, **1**, 427 (1933).

[4] Bent and Keevil, THIS JOURNAL, **58**, 1367 (1936).

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

reported in the first papers of this series. The purpose of these modifications is to increase the ruggedness and permanence of the apparatus and reduce the number of materials in contact with the liquid or vapor in the reaction vessel. In the earlier apparatus cement was used at various points and thermocouple wires and heater leads were not only exposed to the vapor of the solvent but also subjected to mechanical motion when the capsule was broken. In the present apparatus all wires are enclosed in glass with the exception of the platinum heater wire and a silver lead which may be changed to platinum if desired. No cement is used to hold the heater wire in place or at other points in the apparatus. We are now quite free from any possible solvent action and can use the apparatus for chlorination if desired.

In order to save space only the changes in the apparatus will be mentioned and the figure given in the first paper of this series will be used for reference. The chief alteration consisted in sealing the tube which carries the thermocouple and the heater to the stationary tube above the ground joint "D." Two ring seals are used for this purpose, one just below the tube marked "C" in the original figure and the other just above this side tube. The thermocouple leads then pass through this side tube and down through an annular space to the bottom. The annular space is necessary in order that the magnet may now move a glass rod which passes through the whole length of the apparatus and pushes the capsule "J" out at the bottom and breaks it on the Dewar. The lower side tube, at the left in the original figure, is now used for the heater leads which are sealed through the glass by the method of Cox, Kraus and Fuoss.[6] We have used No. 22 silver wire for part of the lead. The heater has a resistance of 17.845 ohms and is made by winding No. 40 platinum wire on glass supports which hold it out about 1 mm. from the glass tube. This is accomplished by first sealing eight pieces of glass rod 1.8 cm. long and 1 mm. in diameter to the bottom of the tube. Tiny dots of glass are then fused to these rods and the wire wound between the glass dots. By using alternate spaces in winding the wire down from the top the two ends can be anchored at the top and crossing of the wire avoided.

The electrical measurements have also been considerably improved since the report of earlier work. All measurements of temperature and current are made with the aid of a type K potentiometer. By means of appropriate switches the potentiometer can be connected to the thermocouple for the measurement of temperature or to the heater, with the aid of a potential divider, to determine the potential drop across the latter. Another switch connects the potentiometer to a standard resistance in series with the heater, this potential drop giving a measure of the current.

The use of platinum as a heater made necessary an automatic control of the energy input on account of the change in resistance of the platinum with temperature. This is accomplished by putting in series with the heater an external resistance of the same size. The latter coil is made from 13.7 meters (45 ft.) of No. 22 Advance wire which has a very small temperature coefficient and is wound without a core in order to dissipate heat rapidly. This arrangement maintains the energy input constant with a fluctuating resistance provided the voltage supply is constant. This can easily be shown to be true as a first approximation and is due to the fact that as the resistance of the heater increases the current decreases but this is appropriately compensated by an increase in the potential drop across the heater. By measuring the resistance of the heater we were able to calculate its rise in temperature above that of the solvent. Using a current of 0.2 amp. we find the rise in temperature to be about one degree, and the increase in resistance to be about 0.3%. An increase in resistance of 1.0% would have caused a decrease in the power input of only 0.002%. Appropriate calculations of heat loss by thermal conduction in the lead wires indicate that this factor introduces less than 0.2% error. The method of calibrating the apparatus electrically at the end of each run takes care of all constant heat losses.

Materials

Diphenyl Di-biphenylene Ethane.—Phenylbiphenylene carbinol was first prepared according to the directions of Ullmann and von Wurstemberger.[7] This was converted to the chloride according to the method of Gomberg and Cone[8] and the chloride converted to the ethane using the procedure of Dorfman.[5] Since the ethane is much less soluble than the chloride or carbinol, which might be present as impurity, crystallization of the ethane from benzene and washing with solvent gave material of satisfactory purity.

Tetraphenyl Di-α-naphthyl Ethane.—Diphenyl α-naphthyl chloromethane was prepared according to the directions of Halford for preparing triphenyl chloromethane.[9] The chloride was converted to the free radical with lead amalgam using the procedure of Dorfman as for the previous compound.

Experimental Results

Table I gives the experimental data on the heat of oxidation of diphenyl di-biphenylene ethane in benzene as a solvent. The first column gives the weight of the sample and the second the purity of the compound as indicated by the amount of oxygen absorbed. The chief uncertainty in the figure for the impurity arises from the fact that the reaction flask contains a vapor phase which is a mixture of benzene and oxygen and the connecting tube contains pure oxygen. It is impossible to estimate with high precision the volume which is to be considered saturated with benzene when making a correction for the change in vapor pressure of benzene during the course of a run. The value for the purity of the compound is probably good to about 0.5%. The third column gives the heat of oxidation per mole based on the amount of oxygen actually absorbed. This value refers to

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[6] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 750 (1935).

[7] Ullmann and von Wurstemberger, *Ber.*, **37**, 73 (1904).

[8] Gomberg and Cone, *ibid.*, **39**, 2967 (1906).

[9] Halford, THIS JOURNAL, **53**, 105 (1931).

the solid ethane as the reactant and peroxide in solution in benzene as the product of the reaction. The next column gives a small correction which it seemed proper to add for the heat of solution of unreacting material. The heat of solution of the ethane is found to be 4.6 ± 0.3 kcal. per mole. If we assume that the material which did not add oxygen has the same heat of solution and make the correction we obtain the values given in the last column of the table. The average given in the last column of the table is obtained by weighting those runs which gave the smoothest curves and thereby permitted the best corrections for heat loss to the surroundings.

TABLE I

HEAT OF OXIDATION OF DIPHENYL DI-BIPHENYLENE ETHANE

Sample, g.	O_2 abs., %	$-\Delta H$ per mole	Correction	$-\Delta H$ corrected
0.4352	96.4	24.05	0.17	24.2
.6600	92.0	22.3	.4	22.7
.5086	97.2	20.25	.13	20.4
.9945	99.5	20.8	.0	20.8
.9905	98.9	22.5	.05	22.55

The heats of solution of the ethane and peroxide have also been determined in order to calculate the value for ΔH when the reaction is carried out either entirely in solution or referred to the solid state. The value for the ethane is 4.6 ± 0.3 kcal. per mole and for the peroxide is 5.4 ± 0.4 kcal. From these figures we obtain the value −26.6 kcal. for the addition of oxygen to the ethane dissolved in benzene to give the peroxide in solution. Similarly if solid ethane is converted to the peroxide the value of ΔH is −27.4 kcal.

The solution of peroxide at the completion of a run was invariably red in color, apparently due to some highly colored substance. As much as 80% of the theoretical amount of white peroxide was obtained from the reaction but all attempts to isolate another compound from the remaining material were unsuccessful. Undoubtedly the yield of peroxide was considerably more than 80% but this was all we were able to isolate, apparently due to the presence of the red colored material which formed an oil when attempts were made to crystallize it.

Tetraphenyl di-α-naphthyl ethane gave results which are less satisfactory. The amount of oxygen absorbed was about 86% of the theoretical amount and the insolubility of the peroxide made it impossible to determine its heat of solution. The results of two representative runs are as follows

Wt. of ethane	O_2 absorbed	ΔH exp.	ΔH corr.
0.3788	85.3	−34.3	−35.3
.8318	87.8	−34.1	−35.1

The values given in the next to the last column are calculated on the basis of the amount of oxygen absorbed and are for the addition of oxygen to solid ethane to give chiefly solid peroxide. A small correction should be made for the heat of solution of the peroxide which remained in solution, about 17 mg. in 150 cc. of benzene. This correction cannot be of much significance, however, due to the very small amount of material involved. A correction should also be applied for the heat of solution of the material which did not react with oxygen. The heat of solution of the ethane is found to be 11 ± 3 kcal. Since this includes the heat of dissociation of part of the material, we have taken a somewhat smaller value for the heat of solution of the material which did not react with oxygen and used this to correct our experimental values and give the values in the last column of the table.

An attempt was made to improve the technique of these oxidation reactions by using pyrogallol as suggested by Ziegler, Ewald and Seib.[10] The results of these experiments were not satisfactory as the amount of oxygen absorbed was less than expected. This may be due to the fact that in our experiments solid ethane is introduced into a solution which contains oxygen. It may be that some of the normal peroxide and some $(C_6H_5)_3$-COOH is formed under these conditions.

Attempts to hydrogenate diphenyl di-biphenylene ethane were unsuccessful. Either the ethane was too insoluble, the rate of hydrogenation was too slow or else the amount of hydrogen absorbed was greater than that expected.

Discussion

The value previously reported for the oxidation of hexaphenylethane is −45.5 ± 0.5 kcal. when the reaction is from solid to solid and −39.3 ± 2.0 kcal. when the reaction is in solution. The values here reported for diphenyl di-biphenylene ethane of −26.6 and −27.4 for the corresponding reactions are so much smaller as to be very striking. The conclusion suggested by these data is that the C–C bond is stronger in diphenyl di-biphenylene ethane than it is in hexaphenylethane by about 20 kcal. This is quite in harmony with the conclusions of our previous papers which indi-

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[10] Ziegler, Ewald and Seib, *Ann.*, **504**, 182 (1933).

cated that the C–C bond in hexaphenylethane is weaker than a normal bond by about 35 kcal., which we attributed to steric hindrance. If one assumes that the C–C bond in hexaphenylethane is a normal bond then there is no way of explaining a bond in diphenyl di-biphenylene ethane which is 20 kcal. stronger. The inference from these data is that steric hindrance is much less when the benzene rings are tied together as they are in this compound, in agreement with the appearance of the model of the molecule.

The surprising result from these experiments is that the decrease in steric hindrance is so large in this compound. If this were the only factor involved in the dissociation of the ethane it would be impossible to explain the fact that the difference in the free energy of dissociation of this compound and hexaphenylethane is only three or four kcal. A solution to the problem is possible if one assumes that phenyl fluoryl has a much larger resonance energy than triphenylmethyl, thereby canceling to some extent the increased strength of the bond in diphenyl di-biphenylene ethane. This is just the opposite of the conclusion reached by Pauling and Wheland in their discussion of this compound.

The above conclusions are based on data involving materials in solution or in the solid state. A much more satisfactory treatment would be based on reactions in the vapor phase. We hope to have some such data to report in the near future but since this work is being interrupted for the present it seems desirable to report the progress which has been made to this time.

In comparing tetraphenyl di-α-naphthyl ethane with hexaphenylethane we are dealing with a difference in heats of oxidation which is not as large as in the case just discussed and therefore the interpretation is more in doubt. Since we have no data on the heat of solution of the peroxide it will not be possible to study this reaction in the vapor phase by the method which we are using with hexaphenylethane.

Summary

1. The heat of oxidation of diphenyl di-biphenylene ethane is found to be about 20 kcal. less than that of hexaphenylethane.

2. This datum indicates that steric hindrance is less than in the case of hexaphenylethane and that the free radical formed by dissociation, phenyl fluoryl, has more resonance energy than triphenylmethyl.

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[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA]

Antioxidants and the Autoxidation of Fats. VI. Inhibitols[1]

BY H. S. OLCOTT AND H. A. MATTILL

Previous work from this Laboratory[2,3,4] has demonstrated that the unsaponifiable lipid fractions of vegetables and vegetable oils contain compounds which are active antioxidants toward lard. It is proposed to call these compounds as a class "inhibitols," a name which indicates their function as inhibitors and also the invariable occurrence of hydroxyl groups, upon which their inhibiting action depends. Although concentrates have been prepared from various sources,[5] only the lettuce inhibitol has been crystallized.[3] The present paper contains a description of the preparation and properties of the inhibitol concentrates from wheat germ, cottonseed and palm oils.

The method used for obtaining the most active concentrates from wheat germ or cottonseed oil is exactly the same as that described for obtaining vitamin E concentrates.[6] Indeed, the physical and chemical properties of vitamin E

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[1] Presented at the Kansas City meeting of the American Chemical Society, April, 1936.

[2] H. A. Mattill and B. Crawford, *Ind. Eng. Chem.*, **22**, 341 (1930).

[3] H. S. Olcott and H. A. Mattill, *J. Biol. Chem.*, **93**, 59, 65 (1931).

[4] E. M. Bradway and H. A. Mattill, THIS JOURNAL, **56**, 2405 (1934).

[5] Inhibitols are present in lettuce, tomatoes, carrots, alfalfa, spinach; in wheat germ, cottonseed, corn, sesame, palm, soy bean and peanut oils; and probably in many other vegetable substances. No demonstrable amounts of inhibitols are present in yeast, lard; or in olive (trace), cod-liver, palm kernel or castor oils.

[6] H. S. Olcott and H. A. Mattill, *J. Biol. Chem.*, **104**, 423 (1934).