silver ion is not changing much in concentration, for example, through dismutation into unipositive and tripositive silver ions.

Furthermore, the rate of change of the potential with the silver concentrations is shown to be inconsistent with the assumption that the argentic silver is wholly or mainly tripositive. This confirms by a fourth method the conclusion that it is mainly bipositive, already drawn from three types of experiments in the preceding article, and shows that this is true even in nitric acid as dilute as 1 to 4 *N*.

The significance of this value in determining the behavior of argentic salts toward other strong oxidizing agents is considered in many of its different aspects. Of special interest seems the hypothesis that argentic silver and the higher oxidation states of other elements are decomposed by water with evolution of oxygen because of the tendency to form hydrogen peroxide, and hence only when their oxidation potential approaches or exceeds the potential (1.77 volts) of the reaction $H_2O_2 + 2H^+ + 2E^- = 2H_2O(l)$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. VI. The Strength of the Carbon–Carbon Bond in Certain Substituted Dixanthyls

BY HENRY E. BENT AND EARLE S. EBERS

The strength of a carbon–carbon bond has frequently been inferred from the ease with which a reaction takes place to give a sodium addition compound. Thus Conant has distinguished between various classes of compounds by determining the activity of sodium which is required to produce a reaction. For this purpose the three materials which have been used are dilute sodium amalgam, 40% sodium amalgam, which is liquid at room temperature, and sodium–potassium alloy.[1] Whether sodium or potassium has been the reactive material in the alloy has usually not been determined. The investigation of concentrated sodium amalgams by Gilfillan[2] indicates that the activity of sodium in 40% amalgam is the same as that of the pure metal in the solid state at the same temperature. Since sodium dissolves readily in sodium–potassium alloy the activity of the sodium in the alloy must be less than that of the solid metal and therefore less than that of sodium in 40% amalgam. The fact that some compounds react with sodium–potassium alloy which do not react with 40% amalgam must therefore be attributed either to the velocity of the reaction or more probably to the fact that the potassium is the reactive metal in the alloy.

The previous papers of this series have shown that the free energy change associated with the addition of sodium to an organic free radical is very little affected by the nature of the various groups attached to the central carbon atom. The maximum range in the values for the free energy change is 6 kcal. If we consider, however, the effect of changing only one substituent at a time on the central carbon we find that this produces a change of not more than 1 kcal. This fact makes it possible to calculate the strength of the carbon–carbon bond in compounds which are not appreciably dissociated into free radicals providing an equilibrium can be established with a dilute sodium amalgam in which the activity of sodium is known. The increase in the activity of the sodium necessary to cause addition to the carbon–carbon bond will then be a measure of the strength of that bond.

For the purposes of this investigation the xanthyl series was chosen. Compounds of this series have been studied by Conant and co-workers.[3] Many of them are not appreciably dissociated at room temperatures but give evidence of dissociation as the temperature is raised. The substituents which have been considered by Conant and co-workers were aliphatic groups and it became imperative to study at least one free radical containing an aliphatic group in order to determine the effect on the electron affinity of this group. Fortunately Conant, Small and Sloan[4] found that diisopropyldixanthyl is almost completely disso-

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(1) Conant and Garvey, THIS JOURNAL, **49**, 2599 (1927).

(2) Gilfillan and Bent, *ibid.*, **56**, 1505 (1934).

(3) Conant and co-workers, *ibid.*, **47**, 572, 3068 (1925); **48**, 1743 (1926); **49**, 2080 (1927); **51**, 1925 (1929).

(4) Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).

ciated at room temperature. The free radical has never been isolated in the solid state but the intense color of the solution and its great reactivity clearly indicate that the free radical is only slightly associated.

We have found a slightly smaller electron affinity for isopropylxanthyl than for any compound previously studied. With the aid of this value we have studied di-*n*-butyldixanthyl, diphenylethyldixanthyl and dibenzyldixanthyl. From the concentration of the sodium amalgam in equilibrium with a mixture of the dixanthyl and the sodium addition compound the free energy of dissociation has been calculated. Assuming that the entropy of dissociation is the same for all free radicals, as has been done by Conant,[5] the heat of dissociation can be calculated. This is accomplished by setting the difference in the free energy of dissociation of hexaphenylethane and the dixanthyl derivative as equal to the difference in the heats of dissociation of the two compounds. The heat of dissociation of hexaphenylethane has been found by Ziegler, thus permitting not only a relative but also an absolute value to be assigned to the strength of the carbon–carbon bond for these dixanthyl derivatives.

Experimental

The experimental method of establishing equilibrium with sodium amalgam had to be modified somewhat in studying compounds of the dixanthyl series on account of various difficulties which we encountered. In the first place diisopropyldixanthyl has never been isolated but has been obtained only in solution. This made it necessary to analyze in some way the solution in order to determine the amount of free radical present. Furthermore, the free radical is very sensitive to light and probably decomposes somewhat even in the dark. This may account for the failure of previous attempts to isolate the compound. We attacked the problem by first preparing the perchlorate salt. This compound is relatively stable and is prepared, according to the directions of Conant, Small and Sloan,[6] by treating the carbinol with perchloric acid. Satisfactory results were obtained only after preliminary careful purification of the carbinol. On treating the perchlorate salt with 40% sodium amalgam and titrating the solution of the sodium addition compound so formed with dilute acid one equivalent of sodium was found.

The determination of the equilibrium constant consists in first preparing the sodium derivative by shaking the salt, in this case the perchlorate, with sodium amalgam. We found no difficulty in obtaining a quantitative reaction when using 40% amalgam. However, attempts to use a dilute amalgam were unsuccessful, probably due to the fact that the reaction did not go to completion and the free radical present was decomposed. This decomposition tended to reverse the reaction and therefore to give, on titrating with dilute acid, much less than one equivalent of sodium. After preparing the sodium derivative the next step is to shake the solution with an amalgam in which the activity of sodium is such that approximately half of the sodium is removed. Again we encountered the difficulty that the free radical so formed partially decomposed. Not being able to prevent the decomposition we corrected our results by measuring the amount of decomposition. This was done by pouring the ether solution at the completion of a determination onto 40% sodium amalgam. This converted all of the material to the sodium derivative and a titration with acid then gave the amount of undecomposed compound. A titration of the very dilute amalgam which was in equilibrium with equivalent amounts of free radical and sodium derivative gave the activity of the sodium. Since the proper amount of pure mercury had been added to the sodium derivative to give this amalgam, this analysis also gave the amount of sodium removed as reported in the first column of Table I. This quantity subtracted from the final amount of undecomposed material gave the quantity reported in the second column of Table I. Further details of the calculations are given in earlier papers of this series.

TABLE I

EQUILIBRIUM DATA FOR THE ADDITION OF SODIUM TO ISOPROPYLXANTHYL

G. atoms Na removed $\times 10^4$[a]	G. atoms Na left $\times 10^4$	Moles of ether	G. atoms of mercury	% decomposed during run	Log K_2 $K_1 = \infty$ $K_3 = 10^{-4}$	ΔF° kcal.
3.19	1.53	1.068	0.1530	68	10.12	
7.26	4.01	1.51	.1530	23	10.39	
9.61	3.56	1.388	.1527	10	10.19	
10.21	3.42	1.370	.1527	8	10.14	
				Average	10.21	−13.94

[a] This figure has been corrected for the amount of decomposition which took place during a run as given in the fifth column of the table.

The meaning of the symbols is the same as in earlier papers of this series. K refers to an equilibrium constant and R represents a free radical:

K_1 is for the reaction $R_2 \longrightarrow 2R$

K_2 is for the reaction $Na + R \longrightarrow Na^+ + R^-$

K_3 is for the reaction $NaR \longrightarrow Na^+ + R^-$

ΔF° in this table is calculated from K_2 by the relation $\Delta F^\circ = -RT \ln K$. Concentrations are expressed as mole fractions.

Dibenzyldixanthyl.—Two modifications of our method were necessary in studying this compound. In the first place the sodium salt was found to be very insoluble in

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

(6) Conant, Small and Sloan, *loc. cit.*

ether, necessitating the use of large volumes of ether. In the second place the reaction is very slow, necessitating shaking for days in order to obtain, even approximately, equilibrium conditions. This is probably due to the fact that as the strength of the bond increases the activation energy for the reaction also increases. On account of the slowness of the reaction it seemed especially desirable to approach the equilibrium from both sides. In two runs the purity of the perchlorate salt was established by shaking with 40% amalgam and titrating the resulting solution with acid. In three runs the solution was first shaken with 40% amalgam and then with dilute amalgam. In two runs the perchlorate salt was treated only with dilute amalgam. Values for the equilibrium constant as calculated from these data indicate that with long shaking equilibrium is approached from both sides. The data are recorded in Table II. The directions for the preparation of the perchlorate were those of Conant and Sloan,[7] using purified carbinol.

TABLE II

EQUILIBRIUM DATA FOR THE ADDITION OF SODIUM TO DIBENZYLDIXANTHYL AND THE DISSOCIATION CONSTANT OF DIBENZYLDIXANTHYL

G. atoms Na removed $\times 10^{4}$[a]	G. atoms Na left $\times 10^{4}$	Moles of ether	Log concn. Na in amalgam	Concn. of free radical $\times 10^{6}$	$K_1 \times 10^{8}$	ΔF kcal.
1.60	0.802	1.80	−1.29	1.74	2.12	10.5
1.335	.660	1.65	−1.28	1.21	1.34	10.7
1.563	.387	2.005	−1.28	0.448	0.129	12.1
1.366	.600	1.845	−1.28	.983	.39	11.1
1.517	.321	1.883	−1.28	.341	.081	12.4
					Average	11.4

[a] In runs 1, 2 and 4 the sodium derivative was first prepared by shaking with 40% amalgam which causes the reaction to go to completion. The first column of the table gives the amount of sodium removed by an amalgam whose mole fraction is given in the fourth column. Runs 3 and 5 approached the equilibrium from the opposite side by shaking directly with an amalgam of the concentration given in column four. For these runs the second column gives the amount of sodium which reacted with the dibenzyldixanthyl and the first column the additional amount of sodium which would have reacted if the reaction had gone to completion.

K_1 is for the reaction $R_2 \longrightarrow 2R$ (R representing the free radical). In calculating K_1 the value for K_2, for the reaction $Na + R \longrightarrow Na^+ + R^-$, has been taken as 10.21 as reported in Table I. ΔF in this table refers to the reaction $R_2 \longrightarrow 2R$.

Di-*n*-butyldixanthyl.—Considerable difficulty was encountered in preparing samples of this compound which would react with 40% sodium amalgam to give the theoretical amount of sodium. The best sample which was used in runs 1–3 neutralized 98% of the calculated amount of acid. Runs 1 and 2 were shaken for two and three months, respectively, with dilute amalgam. Run 3 was shaken first with 40% amalgam and then with dilute amalgam. Run 4 was carried out with a sample of the perchlorate salt, shaking first with 40% amalgam and then with dilute amalgam. The values given for the free energy change are calculated assuming that the free energy change for the addition of sodium to the free radical is the same as that for isopropylxanthyl. The value for ΔF refers to the dissociation of the dixanthyl derivative into the free radical. The preparation of the free radical and the perchlorate salt was according to the directions of Conant and Sloan.

TABLE III

EQUILIBRIUM DATA FOR THE ADDITION OF SODIUM TO DI-*n*-BUTYLDIXANTHYL AND THE CALCULATED VALUES FOR THE DISSOCIATION CONSTANT OF DI-*n*-BUTYLDIXANTHYL

G. atoms Na removed $\times 10^{4}$[a]	G. atoms Na left $\times 10^{4}$	Moles of ether	Log concn. Na in amalgam	Concn. of free radical $\times 10^{6}$	$K_1 \times 10^{8}$	ΔF kcal.
1.608	0.132	0.136	−1.29	0.44	1.88	10.6
1.610	.100	.131	−1.28	.27	0.69	11.1
1.087	.208	.146	−1.28	.76	7.4	9.7
1.674	.606	.151	−1.28	2.95	70.0	8.4
					Best value	10.1

[a] In runs 1 and 2 the equilibrium was approached using dilute amalgam. The figure given in the first column is in these runs the amount of di-*n*-butyldixanthyl which did not add sodium and the figure in the second column the amount of sodium which was added. In the last two runs the sodium derivative was first prepared with concentrated amalgam and then the sodium partially removed with dilute amalgam. The last value probably indicates that equilibrium had not been attained after a period of three days shaking. The first two runs involved shaking for two and three months, respectively.

K_1 and ΔF are calculated as described in the footnote to Table II. They refer to the reaction $R_2 \longrightarrow 2R$ (R representing the free radical).

TABLE IV

EFFECT OF TEMPERATURE ON THE CALCULATED VALUES OF ΔF FOR THE ADDITION OF SODIUM TO TRIPHENYLMETHYL

Temp., of run, °C.	Calcd. value of ΔF
26.5	17.90
26.5	17.90
1.0	18.86
0.5	18.97

Variation in ΔF, kcal./°C. = 0.04.

Diphenylethyldixanthyl.—This compound was prepared according to the directions of Conant and Sloan. The reaction seemed particularly sluggish and at no time did we obtain as consistent results as with the two compounds previously discussed. The data obtained (which are not given) indicate that there is little difference in the strength of the carbon–carbon bond in diphenylethyldixanthyl and the other two compounds studied in this series. Since one would expect the effect of the phenylethyl group to be intermediate when compared with benzyl and *n*-butyl and since these last two compounds differed very little from each other, it did not seem worth while to study this compound further.

The great length of time required to reach equilibrium in many of the above runs caused us to dispense with a

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(7) Conant and Sloan, THIS JOURNAL, **47**, 572 (1925).

thermostat. In order to prove that the reaction has a small temperature coefficient and therefore to justify this procedure four runs were carried out on hexaphenylethane, two at room temperature and two near zero degrees. The values of ΔF were then calculated as though the analytical data had been obtained at 25°. As is evident from the table the temperature coefficient is so small as to make a variation of two or three degrees in the room temperature insignificant. We hope later to calculate the heat of the reaction when we have more data available on the amalgam and the temperature coefficient of the ionization constant of the sodium addition compound.

Discussion

The values of ΔF for the dissociation of dibenzyldixanthyl and di-*n*-butyldixanthyl into free radicals may now be compared with the corresponding value for hexaphenylethane. If we make the very probable assumption that the value for ΔS for the dissociation reaction is the same for all free radicals, as has been done by Conant,[8] then we may write $\Delta F_2 - \Delta F_1 = \Delta H_2 - H_1$. The value of ΔF for hexaphenylethane calculated from Ziegler's[9] data is 5.5 kcal. and ΔH is 11 kcal. From these values we calculate 17 kcal. for the heat of dissociation of the carbon–carbon bond in dibenzyldixanthyl and 16 kcal. for di-*n*-butyldixanthyl. The first of these values is in remarkably good agreement with the value 16.5 given by Conant, based on the temperature at which color could first be observed. The value of 16 kcal. for di-*n*-butyldixanthyl is to be compared with Conant's value of 18.4 kcal. The agreement in both cases is entirely satisfactory considering the assumptions involved in the calculations.

We are now in a position to discuss the fundamental question of the nature of the carbon–carbon bond in ethanes which are capable of dissociation into free radicals. Two fundamentally different explanations have been given serious consideration by various authors. First we have those theories which account for the phenomenon of dissociation by assuming that the carbon–carbon bond is abnormally weak. And, second, we have the more recent explanation given by Pauling and Wheland[10] and by Hückel[11] which assumes that the carbon–carbon bond is quite normal and that the dissociation is to be accounted for by the stabilizing effect of the large resonance energy of the free radical.

In the discussion of this subject by Pauling and Wheland the influence of secondary and tertiary alkyl groups in promoting dissociation was attributed to a steric effect. This was hardly satisfactory as there is no obvious reason for attributing a steric effect to an isopropyl group and not to a phenyl or naphthyl group. More recently Wheland[12] has considered this problem again and suggested that this inconsistency can be avoided by postulating resonance energy in the aliphatic hydrocarbons. As it is not possible at present to calculate the magnitude of this resonance energy, we must look to experimental data for a test of this point.

If the resonance energy of an isopropyl group should turn out to be much smaller than that of a phenyl group, as seems quite possible, this would bring us right back to the position taken in the first paper by Pauling and Wheland, namely, that the steric factor must be important in the case of isopropyl and tertiary butyl groups. But if important here it would seem probable that it should also be considered in the case of aromatic groups. This then leads to the conclusion that the bond in hexaphenylethane is somewhat weaker than a normal carbon–carbon bond as a result of this steric effect and that the phenomenon of dissociation is to be explained by the combination of this influence with that of resonance.

The relative importance of these two factors may be determined by a consideration of thermal data. There are two ways in which one may calculate the weakening of the bond in hexaphenylethane. The first method is to compare the observed heat of combustion of hexaphenylethane with the value calculated by the equations of Kharasch.[13] These equations are found to agree with the experimental values of the heat of combustion quite closely for the various phenylethanes with the exception of hexaphenylethane. In this case the observed value is 4757 kcal. and the calculated value is 4720 kcal. The difference, 37 kcal., may be taken as the weakening of the carbon–carbon bond produced by the introduction of six phenyl groups.

A second method of arriving at this quantity is to compare the heat of combustion of hexaphenylethane with that for two molecules of triphenylmethane. The difference can be calculated with the aid of Pauling's values for the single bond energies and the other thermal data

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[8] Conant, *loc. cit.*

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

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

[11] Hückel, *Z. Physik*, **83**, 632 (1933).

[12] Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

[13] Kharasch, *Bur. Stand. J. Research*, **2**, 359 (1929).

given in Table V. The fact that these two methods agree so closely is quite fortuitous. All of the experimental evidence discussed, however, indicates quite clearly that the bond in hexaphenylethane, and probably in other ethanes which dissociate to give free radicals, is weaker than a normal bond. The thermodynamic data give no explanation of this effect but one might infer that the bulk of the substituents is important in many cases in preventing the carbon atoms from coming close enough together to give a normal bond.

TABLE V

CALCULATED DIFFERENCE IN THE HEAT OF COMBUSTION OF HEXAPHENYLETHANE AND TRIPHENYLMETHANE

Increase for C–C bond	84 kcal.
Adding molecular hydrogen	68
Dissociation of hydrogen	102
Formation of two H–C bonds	−198
Total	56
Experimental value	20
Weakening of C–C bond due to introduction of six phenyl groups	36 kcal.

Summary

1. ΔF for the addition of sodium to dibenzyldixanthyl, diphenylethyldixanthyl and di-n-butyldixanthyl has been determined.

2. From the values for ΔF the heat of dissociation of the carbon–carbon bond in these compounds is calculated to be from 16–17 kcal.

3. The variability of single bond energies is discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Chemical Reactions of Water Adsorbed on Glass

BY H. E. BENT AND G. J. LESNICK[1]

The water adsorbed on glass has been shown to be made up of two parts. First there is water which may readily be removed by pumping and which is held very loosely.[2] Secondly, there is water which is held very firmly and can be driven off by heating to a high temperature while the apparatus is evacuated.[3] It is with the second kind of water that this paper is particularly concerned.

We became interested in this problem because of the need of a clean glass surface in studying quantitatively certain reactions of organic free radicals. Some of the materials involved are so reactive that it seemed quite possible that they would be destroyed by water held so firmly by the glass as not to be removed by pumping, sparking and baking. The method which we have used, therefore, has had to be a chemical rather than a physical means of measuring the adsorbed water. We have used the sodium addition compound of triphenylmethyl as the means of removing adsorbed water. This compound has an intense red color when present in very small concentrations in ethyl ether, reacts rapidly with water and gives products, triphenylmethane and sodium hydroxide, which are colorless. Hence the compound serves as its own indicator. The method has three very distinct advantages as compared with physical methods of measuring adsorbed water. In the first place it duplicates closely the conditions under which chemical experiments might be affected by adsorbed water. In the second place it makes possible the measuring of the amount of water which is very firmly held by the glass. And finally one can study the rate at which the water is liberated over long periods of time. The chief disadvantage is that the method is rather slow and tedious.

Procedure

In carrying out a run the tube to be studied was first sealed onto the vacuum line and exhausted at a pressure of less than 10^{-3} mm. In case the tube was to be heated during evacuation it was surrounded by a vapor-bath of diphenylamine which maintained the temperature at approximately 304°. After cooling, a stopcock was opened to the ether flask in order to prevent change in concentration of the solution of sodium triphenylmethyl when this solution was added. In some cases ether was also distilled into the system in order to obtain the desired volume of solution. The apparatus was then chilled, to prevent decomposition of the ether while sealing off, and the tube and buret sealed off from the pump. After again coming to room temperature the magnetic hammer was

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[1] A thesis submitted in partial fulfilment of the requirements for the S.B. degree in Harvard College with honors in Biochemistry.

[2] Frank, *J. Phys. Chem.*, **33**, 970 (1929); Lenher, *J. Chem. Soc.*, 1785 (1926); Frazer, *Phys. Rev.*, **33**, 97 (1929).

[3] Sherwood, THIS JOURNAL, **40**, 1645 (1918).