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).

raised and the capsule broken. This allowed the sodium triphenylmethyl solution to run down into a buret. A small portion of the solution was poured, by tipping the whole apparatus, into the large tube. If the color was completely destroyed more was added in small portions until a slight color remained. The difference in volume read on the buret then permitted one to calculate the number of moles of sodium triphenylmethyl added and hence the amount of water removed from the glass. As will be observed from the table, the greater part of the water is liberated rapidly but a considerable portion is liberated slowly, coming out of the glass after many days standing in contact with the colored solution. These metal addition compounds are not sensitive to light, as is the case with free radicals, no observable decomposition taking place after exposing solutions to the light for many years.

Materials

In order to give results of value in handling organic free radicals and similar compounds no attempt was made to produce a plane glass surface. Ordinary Pyrex tubing was first cleaned with chromic acid solution, washed thoroughly with distilled water and then allowed to stand full of distilled water for at least a week.

The ether was stored in a flask attached directly to the line and contained the sodium addition compound of benzophenone. The intense blue color of this solution was a guarantee of the absence of water.

The sodium triphenylmethyl was prepared from triphenylchloromethane by shaking with sodium amalgam. The solution was poured into capsules with small tips which were later broken by magnetic hammers. The concentration was computed from the original weight of chloromethane. This was shown to be reliable by a test titration of the solution with acid.

Experiments at Room Temperature

A series of experiments was first carried out at room temperature. The results so obtained are not only interesting in themselves but are necessary in order to apply certain corrections to the results obtained when the tube was heated to 304°. The experimental data were converted to the thickness of a water layer expressed in terms of the number of molecules of water by dividing the number of moles of sodium triphenylmethyl by the area of the tube and multiplying by 5.81×10^8. This assumes that the destruction of the sodium triphenylmethyl is due entirely to water and that the volume of the water molecule is the same as that in liquid water. The results are significant, even in the most favorable conditions, to only about a half molecule of water.

There are a number of factors which contribute to the experimental error. Perhaps the most serious of these is the variation in the surface of the glass from tube to tube and even in the same tube during successive runs. This variation is sufficiently large to justify the rather crude method of titrating, namely, that of pouring solution from the buret into the large tube. A second limitation arises in connection with the intensity of the color of sodium triphenylmethyl. In the dilutions employed in these experiments the amount of solution necessary to produce the first observable color corresponded to about half a molecule. Finally, in considering the significance of the time factor during a given titration it must be borne in mind that the figures are minimum values for the amount of water which can be removed. In order to obtain maximum values it would be necessary to attend the tubes constantly day and night and at all times have a slight color due to the presence of the sodium triphenylmethyl. As actually carried out the solutions were colored most of the time. However, frequently on arriving at the laboratory first thing in the morning the solutions would be found to be colorless, indicating that for an indeterminate length of time the glass had not been in contact with dry ether.

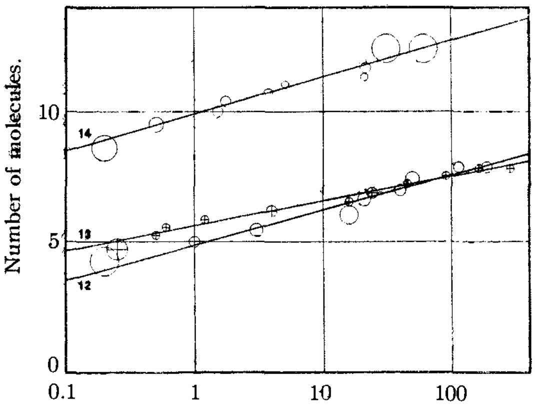

Fig. 1.

Experiments at room temperature indicated that both the time of evacuation and also the time of titration were important in determining the amount of water liberated by the glass. Figure 1 is typical of the results obtained. Runs 12 and 14 were carried out on the same bulb. In the former case the bulb was evacuated for four hours and a half and in the latter three-quarters of an hour. Some time was consumed in sealing off the pump so that perhaps better values would be five and a half hours evacuation for Run 12 and one and a quarter hours for Run 14. The fact that the two curves are parallel indicates that the sodium triphenylmethyl removes almost instantly the water which would have been removed by four hours of pumping, namely, a layer about five molecules thick. These curves also demonstrate that with even so powerful a reagent as that used in the titration some water is removed but slowly. This is strong evidence for the idea that some of the water is dissolved in the glass and diffuses very slowly. The thickness of glass involved in this diffusion may be very small, perhaps only the layer affected by the cleaning solution and left in an abnormal condition. In order to determine whether or not water diffuses through considerable thicknesses of glass, thin tubes of sodium triphenylmethyl have been sealed in larger tubes, on the one hand containing water and the other hand containing phosphorus pentoxide. In the course of more than a year the amount of water diffusing through the glass has not been enough to produce any noticeable difference in the tubes.

In order to summarize the work at room temperature, which consisted of fourteen runs, the equation $n = 5(0.25 \log_{10} t + 1)$ may be used. This is entirely empirical but is convenient and permits the comparison of this work with that now to be described at higher temperatures. In this equation n is the thickness of the water layer in molecules and t is the titration time in hours assuming that the apparatus has been evacuated for one hour before the titration is started.

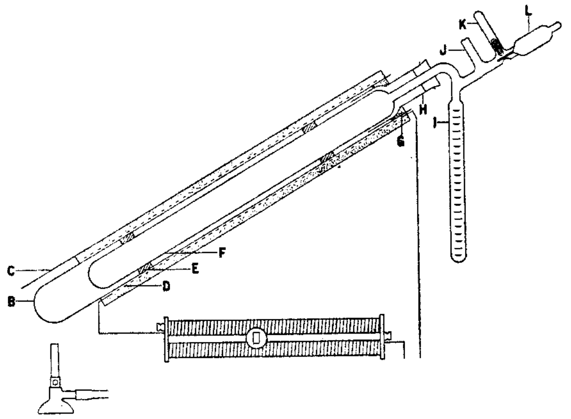

Fig. 2.

Heat Treatment at 304°

Following the runs at room temperature a series was carried out in which the glass was heated by boiling diphenylamine to 304° during the evacuation. The following factors seem to be of importance: the nature of the glass, the length of time it has been in contact with water before the run is started, the length of time the glass is heated, and the length of time for the titration. The limited amount of time available for the problem made possible only a few experiments to test each of these factors. The experimental results are given in Table I. The smaller amount of water held by the glass made necessary the use of dilute solutions for the titration and this is probably responsible for part of the experimental error. The equation $n = (2/T)1/2(0.25 \log t + 1)$ has been chosen to represent the data. Run 28 gives results which are considerably higher than those given by the equation. This may be due to uncertainty in the time of pumping, which was rather short. Any error in technique such as a leak in the system would give high results. For this reason Run 28 should probably not be given much weight. All of the very low results were obtained on bulb number 3. This suggests that there may be a difference in the nature of the glass which persists after cleaning with hot dichromate solution and after many runs. If we calculate the average deviation of the experimental results from those given by the equation, omitting Run 28 and the runs on bulb 3, we obtain a value of 0.3 molecule.

Table I

The Amount of Water Remaining on Glass after Heating to 304°

Run	Heating time	Bulb	Titration time in hours			
			1	4	16	64
28	0:30	4	4.2–5.4	4.2–5.4	5.7–6.0	6.0–6.7
38	0:32	5	2.8–3.0	2.8–3.0	3.0–3.8	4.2–4.7
40	0:38	3	1.3–1.6	1.6–1.9	1.6–1.9	2.7
39	1:15	8	2.7–3.1	3.1–3.3	3.3–3.4	3.6–3.8
31	1:30	3	1.4–1.6	1.4–1.6	1.6–2.3	2.3–3.0
22	2:10	3	0.3–0.8	0.3–0.8	0.3–0.8	0.3–0.8
33	2:10	5	1.1–1.3	1.3–1.9	1.3–1.9	1.9–2.0
37	4:20	4	0.6–0.7	0.7–1.2	0.7–1.2	0.7–1.2
26	5:00	2	.9–1.3	.9–1.3	1.3–2.1	

Comparing the results obtained from tubes heated to 304° with those at room temperature we find that one hour of pumping and one hour titration gives at room temperature a layer five molecules thick, while the higher temperature reduces this to about two molecules. We had hoped to carry on experiments baking the glass at much higher temperatures but the limited time available for the problem and the tedious nature of the runs made this impossible.

The Effect of Ether

Previous work[4] has indicated that ether is effective in removing water. In order to test this

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[4] Bent and Dorfman, This Journal, **54**, 1396 (1932).

point ether vapor was admitted to several tubes before titrating and pumped out before introducing the solution of sodium triphenylmethyl. Apparently the vapor does not remove water. An apparatus was then designed to permit ether from the sodium triphenylmethyl solution to be evaporated and condensed on the surface of the glass to be tested. The condensate was collected in a small bulb in which it was titrated. The data indicate that dry liquid ether will remove about half as much water as is removed by heating to 304° for two hours.

The Vapor Pressure of Water on Glass Dried by Sodium Triphenylmethyl

In order to compare the amount of water removed by sodium triphenylmethyl with the amount removed by heating and evacuation, one should know the vapor pressure of water which would be in equilibrium with sodium triphenylmethyl. In other words one should have a value for the free energy change for the reaction

$$NaR + H_2O = NaOH + RH \qquad (1)$$

in which "R" represents triphenylmethyl. ΔF for this reaction, all materials being dissolved in ether, would enable one to calculate immediately the activity of the water which would be in equilibrium with the ether solution.

The value for the free energy change for reaction (1) may be obtained by summing up the equations

	ΔF kcal.	
$NaR = Na + R$	−23.4	(2)
$Na + H_2O = NaOH_{solid} + {}^1/_2H_2$	−34.2	(3)
$R + {}^1/_2H_2 = RH$	− 8.0	(4)
Sum	−18.8	

The value for equation (2) is obtained from equilibrium measurements on sodium triphenylmethyl and mercury. Since[5] there are the same number of molecules in solution on both sides of the equation until the dilution is so great as to cause appreciable ionization of the sodium triphenylmethyl, this value for the free energy is independent of the concentration of the solution. The sodium is referred to the pure metal as the standard state. The value for equation (3) is obtained by subtracting the free energy of formation of water from that for sodium hydroxide. The latter has been obtained by Shibata.[6] If the complete reaction were given by equations (2) and (3), it is interesting to observe that the free energy change for the combined reaction would be −10.8 kcal., corresponding to a vapor pressure of water of about 10^{-7} millimeter. However, the hydrolysis of sodium triphenylmethyl leads to the formation of triphenylmethane, which makes ΔF for the reaction still more negative. The free energy change for this reaction may be calculated from single bond energies, which give ΔH for the reaction, and the change in entropy for the reaction, which may be estimated. ΔH for the reaction may be obtained from the reactions

	ΔH, kcal.	
${}^1/_2H_2 = H$	+51.2	(5)
$R = R'$	+36.5	(6)
$R' + H = RH$	−99.7	(7)
Giving ${}^1/_2H_2 + R = RH$	−12.0	(8)

The value for reaction (5) is the heat of dissociation of hydrogen. Reaction six involves only the resonance energy of triphenylmethyl due to its odd electron as calculated by Pauling and Wheland. R represents the normal free radical, stabilized by this resonance energy and R′ represents the free radical without this resonance energy. Reaction (7) is the value for the normal hydrogen carbon bond given by Pauling.[7] A somewhat lower value would be more consistent with the work of Kistiakowsky and Gershinowitz. However, in order to be consistent in using Pauling's value for the resonance energy his value for the carbon hydrogen bond has also been used. The sum of reactions (5), (6) and (7) gives the desired reaction (8).

The value for reaction (8) may also be calculated from experimental data on heats of combustion. This may be done by using a smaller value for the resonance energy of triphenylmethyl, calculated from the data of Bent and Ebers[8] or more directly by summing the equations

	ΔH, kcal.	
$2R = R_2$	− 11.0	
R_2 + oxygen = water + carbon dioxide	−4757.0	
H_2 + oxygen = water	− 68.4	
Water + carbon dioxide = 2RH + oxygen	−4777.4	
$2R + H_2 = 2RH$	− 59.0	(8)

The heats of combustion have been determined by Schmidlin.[9] This value is combined below with the ΔS of hydrogenation to give an alternative value for reaction (1). We are conducting

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[5] Bent, This Journal, **52**, 1498 (1930).

[6] Shishakov, *C. A.*, **23**, 5380 (1929).

[7] Pauling, This Journal, **54**, 3570 (1932); *J. Chem. Phys.*, **1**, 362 (1933).

[8] Bent and Ebers, This Journal, **57**, 1242 (1935).

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

experiments in order to measure directly the value for (8) which at present is in such doubt.

ΔS for reaction (8) may be estimated in two different ways. Both methods agree quite well with each other and indicate that the change in entropy is small. The first method rests upon the observation of Parks and Huffman[10] that the addition of hydrogen produces very little change in the entropy of a compound, whether solid, liquid or gas. They estimate an increase in entropy of 2.7 e. u. This combined with the entropy of hydrogen, 31.2, gives a decrease in entropy of about 28.5 e. u. on the addition of a molecule of hydrogen.

Quite a different method of estimating this entropy change is to combine the observation of Conant[11] that the entropy of breaking a carbon–carbon bond to form a free radical is $+ 17$ e. u. with the empirical entropy equations of Parks and Huffman which give for the addition of hydrogen to a solid hydrocarbon (producing two smaller molecules) -13.2 for solids and -6.2 for liquids. The difference between the entropy of hydrogenation and that of dissociation gives the entropy change for the addition of hydrogen to a free radical as -30.2 for solids and -23.2 for liquids. At 25° this gives for $T\Delta S$ from 4.5 to 3.5 kcal., a difference which is not significant for these calculations.

Our final estimate for the free energy change for reaction (4) is then obtained from the relation $\Delta F = \Delta H - T\Delta S$. Using single bond energies and Pauling's value for the resonance energy to calculate ΔH gives -8 kcal. Using heat of combustion data gives -25.5. Putting these values into equation (4) gives for the over-all reaction of hydrolysis of sodium triphenylmethyl a free energy change of -18.8 and -36.3 or a vapor pressure of water from 10^{-12} to 10^{-26} mm. Both of these values are much smaller than can be obtained by evacuation, thus explaining the large amounts of water removed by sodium triphenylmethyl after baking and evacuation. We are inclined to believe that the smaller of these vapor pressures is probably nearer the truth than the larger one.

One might well raise the question as to whether equilibrium is ever attained in this reaction. However, since sodium triphenylmethyl is known to ionize in ether solution to give sodium ion and triphenylmethyl ion a rapid reaction would be expected. Conant and Wheland[12] have shown that reactions with acids which are much weaker than water are rapid, which makes it probable that equilibrium is rapidly attained in this case.

Conclusions

1. The amount of water held on the surface of Pyrex glass after washing with hot chromic acid and rinsing with distilled water may be represented by the equation $n = 5(0.25 \log_{10} t + 1)$. This assumes that the apparatus has been exhausted for an hour. "t" is the time in hours during which the glass has been in contact with sodium triphenylmethyl. "n" is the amount of water removed by the sodium triphenylmethyl expressed as the thickness of the water layer in molecules.

2. The expression $n = (2/T)^{1/2}(0.25 \log_{10} t + 1)$ represents the amount of water removed by sodium triphenylmethyl after baking the apparatus at 304° for the time "T" and treating the surface with sodium triphenylmethyl for the time "t."

3. The vapor pressure of water in equilibrium with sodium triphenylmethyl is estimated to be less than 10^{-12} mm. of mercury and probably of the order of 10^{-26} mm.

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[10] Parks and Huffman, "Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932.

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

[12] Conant and Wheland, THIS JOURN 54 1212 (1932).