as per cent. by weight. Within the limits of our experimental error it is possible for a to be a linear function either of the nitrogen concentration expressed as per cent. by weight, or of the ratio of the number of iron to nitrogen atoms. The values of c, however, are not linear functions of either of these variables. We do not believe that any of the results thus far obtained are sufficiently accurate to warrant the deduction of empirical equations expressing either a or c as functions of the nitrogen concentration.

We wish to acknowledge the excellent coöperation of Miss Ellen Z. Kibbe, who analyzed all the nitride samples, and Mr. Leonardo Testa, glass blower.

Summary

1. The equilibrium data for the reaction $2Fe_4N + 3H_2 = 8Fe + 2NH_3$ have been extended to 400 and 575°; they indicate that the percentage of NH_3 in an NH_3-H_2 mixture at 1 atmosphere necessary to convert Fe to Fe_4N is 37 ± 2 at 400, and 14.5 ± 1 at 575°.

2. The percentages of ammonia in an NH_3-H_2 mixture in equilibrium with the solid phases γ' and ϵ were found to be 77 ± 2 at 400, 70 ± 2 at 444 and 57 ± 1.5 at 500°.

3. The composition and lattice dimensions of the ϵ-phase in equilibrium with various NH_3-H_2 mixtures have been determined at 400 and 444°.
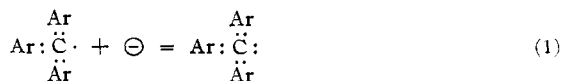
WASHINGTON, D. C

THE ELECTRON AFFINITY OF FREE RADICALS. II. DIPHENYL-ALPHA-NAPHTHYLMETHYL, DIPHENYLBIPHENYL AND PHENYLBIPHENYL-ALPHA-NAPHTHYLMETHYL

BY HENRY E. BENT

The work to be described in this paper is a continuation of the study of the effect of various groups on the electron affinity of organic free radicals.[1] The type reaction may be represented by the equation

$$\text{Ar} : \overset{\text{Ar}}{\underset{\text{Ar}}{\overset{..}{\text{C}}}} \cdot \ + \ \ominus \ = \ \text{Ar} : \overset{\text{Ar}}{\underset{\text{Ar}}{\overset{..}{\text{C}}}} : \qquad (1)$$

Ar, in general, being an aromatic group.

The details of the method and experimental procedure are described in the first paper on triphenylmethyl, in which it was shown that its electron affinity in the gaseous state is 59 kg. cal. with an uncertainty of the order of magnitude of 5 kg. cal. The reaction studied experimentally is the addition of sodium to the free radical to give the negative ion in ether solution

$$Na + R = Na^+ + R^- \qquad (2)$$

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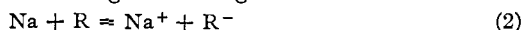
[1] H. E. Bent, THIS JOURNAL, **52**, 1498 (1930).

in which R is the free radical. It is possible to determine the free energy change for this reaction by shaking a solution of the sodium salt with mercury. This partially reverses the reaction and from the equilibrium data the free energy change for Reaction 2 is obtained. By combining appropriate equations an estimate is then obtained for Reaction 1 in the gaseous phase.

This paper describes the work on three more free radicals which were chosen because of the large dissociation of the correspond- ing ethanes and because of their increasing complexity. The large dissociation of the ethane makes it possible to assume in the dilute solutions used that all of the material is in the form of the free radical.

Procedure

The experimental technique has been improved in two or three respects. The final crystallization of the chlo- ride, which is sensitive to moisture, is carried out in an atmosphere of carbon dioxide. A convenient apparatus is made by cutting the bottom from a ten-liter bottle, inverting, and supporting a glass shelf at the beginning of the constriction of the neck. This shelf is put in place by fastening corks to the inside of the bottle with sealing wax melted onto the glass with a soldering iron. Dry carbon dioxide is then passed steadily into the neck of the bottle during recrystallization. Analysis of the gas shows that objects may be moved in and out of the bottle without introducing as much as 1% of air. The purified chloride is transferred to a small bottle without coming in contact with air. This small bottle, Fig. 1, may be evacuated for removal of the last traces of solvent and permits removal of a sample without introducing air. a steady stream of carbon dioxide preventing downward

Fig. 1.—Sample bottle.

diffusion while the sample is removed with the aid of a long silver spatula.

The alundum disks used for filtering the solutions have been replaced by sintered Pyrex disks, which give tighter seals to Pyrex and less adsorption of water or other reactive compounds.[2]

Materials

α-Naphthyldiphenylchloromethane.—This compound was prepared from the corresponding carbinol, obtained from the Eastman Kodak Co., by treating with hydrogen chloride. The chloride so formed melted at 169–171° and the analysis for chlorine by the Carius method gave 10.65 and 10.89; calcd., 10.79.

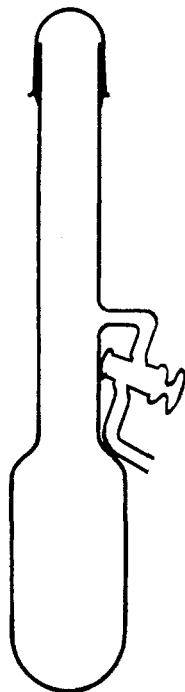   [2] W. F. Bruce and H. E. Bent, THIS JOURNAL, 53, 990 (1931).

Diphenylbiphenylchloromethane.—Dr. R. B. Whitney very kindly furnished this compound. The preparation of benzophenone[3] was carried as far as the chloride stage as the first step. This was then isolated[4] and the final Friedel and Crafts reaction carried out according to the directions of Schlenk.[5] After recrystallization, analysis for chlorine gave 9.75; calcd., 10.0.

Phenylbiphenyl - α - naphthylchloromethane.—Phenylbiphenyl ketone was prepared[6] and converted into the carbinol by means of α-naphthylmagnesium bromide.[7] The chloride was then treated with hydrogen chloride gas as usual and after recrystallization analysis for chlorine gave 8.45 and 8.47; calcd., 8.76.

Experimental Results

The experimental data are given in Table I, the last column giving the mean value of log K for Reaction 2. In the sixth column the calculation is made assuming the salt to be completely ionized, an assumption which,

TABLE I

EQUILIBRIUM CONSTANTS FOR THE ADDITION OF SODIUM TO FREE RADICALS

Compound	G. atoms of Na removed $\times 10^4$	G. atoms of Na left $\times 10^4$	Moles of ether	G. atoms of mercury	Log K_2 $K_3 = \infty$	Log K_2 $K_3 = 10^{-4}$	Mean
Diphenyl-α-naph-	0.750	2.305	0.145	1.01	14.71	13.40[b]	
thylmethyl	.626	1.024	.107	1.387	14.43	13.31	
	.287	0.540	.119	1.250	14.46	13.61	
	.142	.232	.119	1.190	14.31	13.72	
	.137	.234	.120	1.238	14.37	13.78	13.6
Diphenylbiphenyl-	1.608	3.642	.129	1.200	14.58	14.04	
methyl	1.211	2.424	.126	1.151	14.46	14.08	
	0.343	1.203	.143	1.115	14.87	13.80	
	.226	0.749	.134	1.070	14.84	13.91	
	.125	.287	.106	1.560	14.78	14.09	14.0
Phenylbiphenyl-α-	.560	6.39	.102	1.493	16.17	14.32	
naphthylmethyl	.284	1.693	.117	1.192	15.45	14.17	
	.274[a]	1.948	.079	1.829	15.96	14.48	
	.223[a]	1.203	.099	1.065	15.38	14.17	
	.178[a]	1.219	.095	1.106	15.63	14.39	
	.112	0.373	.128	1.437	14.99	14.27	14.30

[a] These runs were made by Mr. M. E. Dorfman on a fresh sample of chloride. [b] The large values of log K_2 arise from the large free energy change accompanying the solution of sodium in dilute amalgam. Log a_2/N_2 for these amalgams is -12.89; see Bent and Hildebrand, THIS JOURNAL, **49**, 3011 (1927).

[3] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 26.

[4] Gomberg, THIS JOURNAL, **37**, 2577 (1915).
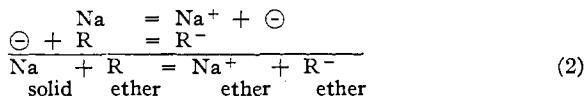
[5] Schlenk, *Ann.*, **372**, 18 (1910).

[6] Norris, Thomas and Brown, *Ber.*, **43**, 2956 (1910).

[7] Schlenk, *Ann.*, **394**, 196 (1912).

of course, is not correct.   The data of this column are given for the purpose of showing to what extent the assumed ionization constant influences the final results.   In the seventh column the value of K_3, the ionization constant of the sodium salt, is taken as 10^{-4}.   This is the same value that was used in the first paper and gives the most concordant results for K_2.   One would hardly expect a variation of more than a power of ten among such similar compounds and anything smaller than this is not significant for these calculations.   Although the assumption that the mass law may be applied to the ionization of these electrolytes in ether solution, using concentration for activities, is certainly not accurate,[8] it probably introduced no significant error which would alter the conclusions.   Only if these compounds deviated widely in their behavior, not only from the simple mass law but also from each other, would the conclusions drawn from these experiments be in error.
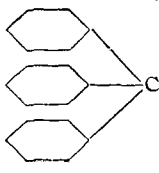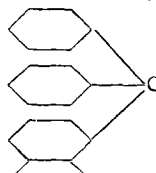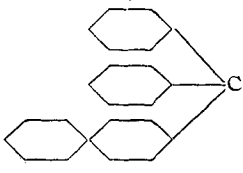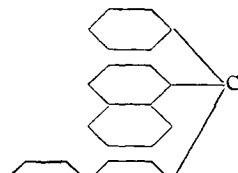
Discussion of Results

The equilibrium constants corresponding to the addition of sodium to four different free radicals have been determined experimentally.   For sodium the standard state is taken as the metal at $25°$.   For the radical and the two ions the activity is taken as equal to the mole fraction.   The total reaction may be considered to be the sum of two reactions: first, sodium metal giving sodium ion and an electron; second, free radical plus an electron giving the methide ion.

$$
\begin{array}{ll}
\text{Na} & = \text{Na}^+ + \ominus \\
\ominus + \text{R} & = \text{R}^- \\
\hline
\text{Na} + \text{R} & = \text{Na}^+ + \text{R}^- \\
\quad\text{solid}\quad\text{ether} & \quad\text{ether}\quad\text{ether}
\end{array}
\tag{2}
$$

The equilibrium constants given in Table I are for this total reaction. In discussing the results it is perhaps more convenient to express them as free energies with the aid of the equation $\Delta F = -RT \ln K$.   Table II gives the values in kilogram calories for ΔF of Reaction 2.

TABLE II

THE FREE ENERGY OF ADDITION OF SODIUM TO FREE RADICALS IN ETHER SOLUTION

Triphenylmethyl	Diphenyl-α-naphthylmethyl	Diphenylbiphenyl-methyl	Phenyl-α-naphthyl-biphenylmethyl

ΔF, -17.9	ΔF, -18.6	ΔF, -19.1	ΔF, -19.5

[8] Ziegler and Wollschitt, *Ann.*, **479**, 123 (1930).

The free energy data given in Table II are, therefore, the sums of the free energy changes for the two parts which go to make up reaction (2). Since, in every case, sodium ion is being formed in ether solution, the energy change corresponding to this part of the reaction will be a constant and any changes in ΔF in Table II must be due to the changing electron affinity of the free radical. In the first paper of this series an estimate of 59 kg. cal. was obtained for the electron affinity of triphenylmethyl in the gaseous state. As far as possible comparisons should be made in the gaseous state in order to eliminate the effect of the solvent. When this is done the variation of 1.6 kg. cal. in the electron affinities of the free radicals studied becomes a little less than 3% of the energy change in the gaseous state. One may say, then, that to a rather rough first approximation the electron affinity of the four free radicals studied is the same.

Further examination of the data leads to the conclusion that within this 3% variation in the electron affinity there are regularities which are significant. An increase in the size of the molecule causes an increased electron affinity. Thus, substitution of an α-naphthyl group for the phenyl group produces a change in ΔF of 0.7 kg. cal., while a substitution of biphenyl for phenyl produces a change of 1.2 kg. cal. The two groups substituted in the same molecule produce an effect which, within the accuracy of the experiments, is the sum of their effects individually, namely, 1.6 kg. cal. The experimental error is about 0.2 kg. cal.

The fact just noted, that the larger molecules have the greater electron affinity, is very surprising when considered in conjunction with the data on the dissociation of the corresponding ethanes. If the energy change accompanying the process of joining two carbon atoms is determined by the behavior of the electrons entering into the bond, then a larger electron affinity might be expected to give rise to a greater strength of chemical bond. For polar compounds this may readily be demonstrated by breaking up the whole process of compound formation into several steps, as has been done by Born, one of which is the addition of an electron to the negative element. It becomes evident in this case that a greater electron affinity, other factors remaining constant, causes the resulting compound to be more stable. The same fact may be observed when considering a series of compounds such as the halogen derivatives of a number of metals. The fluorides are most stable, then the chlorides, bromides and iodides. This is the same order found in measuring the electron affinities of the halogens, fluorine having the greatest and iodine the least electron affinity. The oxides and sulfides show a similar connection. In fact, the phenomenon that the greater electron affinity is associated with the more stable compound seems to be quite general. When we turn to non-polar compounds we find that it is not quite so easy to break up the process of compound formation into a number of steps which are known experi-

mentally. However, here also stability seems to be associated with a large electron affinity. The best illustration is probably to be found in the stability of the halogen molecules, iodine, which dissociates readily, having a small electron affinity and fluorine, which has a large heat of dissociation, having a high electron affinity.

It would appear, therefore, that the electron affinity of an atom or molecule is a measure of the energy change accompanying a process which is very intimately related to chemical valence and the stability of chemical compounds. The two processes, of course, have much in common. In the case of the electron affinity the process involved is the bringing of an electron to a carbon atom which has seven electrons around it, six of which are shared. In the case of the formation of a carbon–carbon bond an electron is brought to the same carbon but, in this case, is not a free electron but is an odd electron of another carbon atom. From the standpoint of these relations one would expect the larger free radicals to be the least dissociated, judging by their electron affinities, which are the greatest. What one finds is that these are the free radicals which are most dissociated. Walden[9] has summarized the various data which all lead to the conclusion that the larger free radicals studied in this work are those which are most dissociated.

The way out of this difficulty seems to be with the aid of the concept of steric hindrance. If we assume that the strength of the bond is determined not alone by the behavior of the electrons forming the valence pair but also by the rest of the molecule, then it is possible to understand the above facts. In Fig. 2, a schematic curve, we may indicate very roughly the potential energy of a system of a free radical and an electron as a function of the distance, r, between them. We may also assume that a free electron approaches to about the same distance from the central carbon atom regardless of the bulk
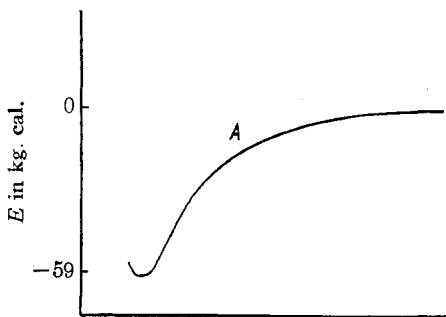

Fig. 2.—The electron affinity as a function of the distance of the electron from the equilibrium position in the molecule.

or exact position of other groups attached to it, the depth of the valley in this potential energy curve being the 59 kg. cal. determined in this investigation. If, however, the electron were attached to a bulky group of atoms we might not be surprised to find that it could approach only to a distance corresponding to the position (A) on the curve, and the decrease in the energy of the system would be correspondingly less. The fact that the

⁹ P. Walden, "Chemie der freien Radikale," Verlag von S. Hirzel, Leipzig, 1924.

larger free radicals have somewhat deeper potential energy curves, therefore, has little effect on the firmness of a weak bond, this being determined primarily by the closeness of approach of the two atoms. Thus, the biphenyl and α-naphthyl groups prevent the central carbon atoms coming as close together as they do when phenyl groups are involved, and the bond is correspondingly weaker.

This idea also explains the fact that the heat of dissociation of the normal aliphatic carbon–carbon bond is about 73 kg. cal.,[10] while the heat of dissociation of the bond in hexaphenylethane is about 11 kg. cal.[11] These figures indicate that the steric effect prevents the two carbon atoms approaching closer than the distance which corresponds to about one-seventh of the way down the potential energy curve for two aliphatic carbon atoms. The fact that the heat of dissociation of ethane is about the same as the value calculated for a single bond in diamond[10] indicates that the hydrogen atoms in ethane introduce, as might be expected, no steric effect.

Two questions remain to be considered: first, the significance of the solvent in these equilibria, and, second, the use of free energy data in discussing the potential energy curve in Fig. 2. Although the conclusions discussed above are found not to be altered by either of these considerations, they can hardly be dismissed without careful attention.

The solvent undoubtedly has a very great effect on the equilibrium studied experimentally. In the paper on triphenylmethyl it was shown that the solvent affected the free energy change of the reaction to the extent of about 77 kg. cal. Since most of this 77 kg. cal. comes in the solvation of the sodium ion, the effect of the ether on the electron affinity of the free radical is very much less. The significant problem, however, is to determine to what extent the effect of the solvent will vary from one compound to another. Considering the reaction

$$R + \ominus = R^-$$

it is necessary to discover in what way the activities will change in passing from the standard state for the solution to the standard state for the gas reaction, and in particular how this change will vary with radicals of varying size. The effect of the solvent may be divided into three parts: first, the change in activity in passing from the standard state in solution to the standard state in the gas resulting from the van der Waals' forces; second, a similar effect resulting from more specific valence forces centering around the unsaturation in the free radical; third, the effect of the solvent resulting from the charge on the ion. The first of these factors, that of van der Waals' forces, does not have to be considered inasmuch as it will be the same for the ion as for the free radical and will, therefore, cancel out.

[10] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1931, p. 328.

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

The second, the effect of valence forces, probably is not significant, inasmuch as Ziegler and Ewald[11] have shown that the change in the dissociation constant and the heat of dissociation of hexaphenylethane, in passing through a series of eight widely varying solvents, varies less than 2 kg. cal. In considering the third factor, the effect of the solvent resulting from the charge on the ion, we find that there is an increase in the free energy in passing from the ion in solution to the ion in the gaseous state.   The amount may be calculated by Born's equation

$$\Delta F = \frac{e^2}{2r} (1 - 1/D)$$

which gives 27 kg. cal. for an ion of radius 4.6 Å.   An increase of 33% in the volume of the ion would cause a decrease of about 2.7 kg. cal. in this free energy change.   This would also result in $-\Delta F$ for the electron affinity of a large free radical in the gaseous state being larger than for a small one as compared with the values in ether solution.   Therefore, we are led to the conclusion that the solvent affects the comparison of free energies to a small extent, 3–5 kg. cal., and that the observation that the larger molecule has the greater electron affinity would be still more marked in the gaseous state.[12]

The second question to be considered is the relation between the free energy change of the gas reaction and the heat of the reaction.   Since the free radical and its ion are of the same mass, by the Sackur–Tetrode equation they will have the same entropy.   The change in entropy for the reaction will be just the entropy of the electron gas which is of the order of three entropy units.   Therefore, for this reaction ΔF equals ΔH to within 1 kg. cal., making use of the equation $\Delta F = \Delta H - T\Delta S$.   Hence for practical purposes we can interchange free energy and heat of reaction in discussing these reactions.

In conclusion, the writer takes pleasure in acknowledging the work of Mr. M. E. Dorfman in making measurements on one of the compounds and the assistance of Dr. R. B. Whitney in preparing another.

[12] A somewhat different way of treating the same problem of the effect of the solvent on the equilibrium is to consider the changes in heat content and entropy of the reactants and products in passing from the solution to the gaseous state.   The changes in entropy of the ion were calculated by the method used by Latimer and Kasper[13] for water solutions taking the experimental data of Bridgeman for the coefficient of thermal expansion of ether and integrating graphically.   The change in entropy of the free radical was estimated from Hildebrand's modification of Trouton's rule and from his definition of regular solutions as being those for which there is no entropy change on mixing. The heat change for the ion was calculated by the equation of Born given above, which is for either heat or free energy change.   The heat of solution of the free radical would be practically the same for both and was estimated from Hildebrand's modification of Trouton's rule and the specific heats.   The result was approximately the same as from the more direct procedure and offers confirmation of that result.

[13] Latimer and Kasper, THIS JOURNAL, 51, 2293 (1929)

Summary

1.   As a first approximation the electron affinity in the gaseous state of the four free radicals studied is 60 kilogram calories.

2.   The substitution of larger groups for phenyl slightly increases the electron affinity.   The effect of substituting two groups is approximately the sum of the effects of the groups individually.

3.   The fact that the larger free radicals have the greater electron affinity and the smaller tendency to form ethanes suggests that due to steric hindrance the carbon atoms cannot approach each other as closely and, therefore, the energy liberated is smaller.

4.   The effect of the solvent on the equilibrium is considered and found to be essentially the same for the four free radicals studied.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THERMODYNAMIC PROPERTIES OF FUSED SOLUTIONS OF SODIUM BROMIDE IN SILVER BROMIDE

BY EDWARD J. SALSTROM

The following investigation represents a contribution to the general program begun by Hildebrand and Ruhle[1] of gathering data upon the free energy of dilution of fused salt solutions.   The system selected, solutions of sodium bromide in silver bromide, is a continuation of the more recent study by Salstrom and Hildebrand[2] of investigating the influence of the size of the cation of the diluting salt upon the activity of the solvent.   The freezing point–composition diagram obtained for this system by Sandonnini and Scarpa[3] shows no evidence of complex salt formations which might add complexity to any interpretation of the results.

Experimental Part

The sodium bromide was from commercial sources of high purity   The remaining materials, apparatus and procedure involved in this investigation were essentially the same as those described for the previous study of lithium bromide in silver bromide.[2,4]   In short, the method consists of removing hydrolysis and oxidation products from the cell by bubbling a stream of dry hydrogen bromide gas through the fused salts for at least two hours.   Bromine gas generated by electrolysis of fused lead bromide

   [1] Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).
   [2] Salstrom and Hildebrand, *ibid.*, **52**, 4650 (1930).
   [3] Sandonnini and Scarpa, *Atti. accad. Lincei*, II, **22**, 517 (1913)
   [4] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930).