addition of ammonium nitrate increases the volume of nitrogen evolved; (3) the addition of sodium hydroxide or potassium nitrate decreases the amount of nitrogen evolved; (4) although nitrogen is produced when less than enough ammonia is present to form the silver diammonia ion, a large excess of ammonia is necessary to give the maximum nitrogen evolution. With still higher ammonia concentrations the amount of nitrogen produced decreases again. (5) Yost, and King were unjustified in assuming that in their experiments the disappearance of persulfate was due to one reaction only.

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THE ELECTRON AFFINITY OF FREE RADICALS. I. THE ELECTRON AFFINITY OF TRIPHENYLMETHYL

BY HENRY E. BENT

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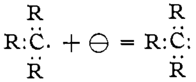
The elementary process of removing an electron from an atom involves an energy change which is related to both the nuclear charge and the electronic configuration of the atom. Millikan and Bowen[1] have shown the energy to be a linear function of the square of the nuclear charge in systems containing the same number of electrons. A study of the electron affinities of free radicals offers the opportunity of keeping the nuclear charge and the number of electrons constant while studying the effect of varying the groups which share six of the electrons of the atom. Thus in the reaction



$$R{:}\underset{\ddot{R}}{\overset{R}{\dot{C}}}\cdot + \ominus = R{:}\underset{\ddot{R}}{\overset{R}{\ddot{C}}}{:}$$

the measurement of ΔH for various radicals should enable one to determine to what extent the addition of an electron to an odd molecule to form an electron pair is affected by a change in the configuration of the rest of the electrons in the molecule. This paper describes the procedure and gives the data for triphenylmethyl.

The reaction chosen for study is that of the addition of sodium to triphenylmethyl

$$Na + R = Na^+ + R^-$$

in which R represents triphenylmethyl. The free energy change accompanying this reaction may be obtained directly from the equilibrium constant for the reaction provided experimental conditions can be found for establishing an equilibrium and determining the activities of the various molecular and ionic species. The large deviation from perfect solution shown by sodium amalgams suggested the possibility of using them in

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[1] Millikan and Bowen, *Proc. Nat. Acad. Sci.*, **13**, 531 (1927).

measuring such equilibria. The activity of sodium in dilute amalgam has been determined recently as a function of the concentration of the amalgam[2] and indicated that sodium amalgams could be used provided the free energy change is of the order of magnitude of 20,000 calories.

The first step is to prove that the reaction is reversible. This was accomplished first by noting that sodium amalgam reacted with triphenylmethyl to give a dark red solution of sodium-triphenylmethyl and that this red color partially disappeared on shaking with mercury and was restored by again shaking with sodium amalgam. Schlenk[3] has recently shown that sodium can be removed from a number of similar compounds by shaking with mercury. As further proof that the reaction is reversible, the equilibrium was approached from both sides and the concentration of the sodium in the amalgam determined by treating with standard acid. Within the limits of the accuracy of the analysis there was no difference between the two results.

A study of the data obtained in this work together with the information which we already have regarding these compounds indicates that there are at least three independent reactions

$$R_2 = 2R \qquad (1)$$
$$Na + R = Na^+ + R^- \qquad (2)$$
$$NaR = Na^+ + R^- \qquad (3)$$

By combining these equations we obtain in addition the following equations

$$Na + R = NaR \qquad (4)$$
$$2Na + R_2 = 2Na^+ + 2R^- \qquad (5)$$
$$2Na + R_2 = 2NaR \qquad (6)$$

Values for the free energy changes for the above reactions have been determined taking the standard state for sodium as the metal at 25°, while for all other molecules or ions the activity has been taken as equal to the mole fraction. Values for the free energy change of Reaction 2, using a number of free radicals, will give the effect of varying valence bonds on the electron affinity inasmuch as the other product is in every case sodium ion in ether.

The absolute value for the electron affinity, however, is to be obtained by studying the reaction in the gaseous state. This may be done by combining the above reaction with the appropriate equations for vaporization, solvation and the ionization potential of sodium to give the electron affinity of triphenylmethyl in the gaseous state. The value so obtained is 59 ± 5 kilogram calories.

Experimental

A weighed amount of triphenylchloromethane is first introduced into a tube (B, Fig. 1) and the apparatus sealed to a line for evacuation. The tube is warmed and sparked during evacuation and the pumping continued

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[2] Bent and Hildebrand, THIS JOURNAL, **49**, 3011 (1927).

[3] Schlenk and co-workers. *Ann.*, **463**, 1 (1928).

until the pressure measured by a McLeod gage is less than 5×10^{-4}mm. A stopcock, not shown, is then opened to allow sodium amalgam to run into Tube B and then a second stopcock through which ether is distilled from a reservoir containing sodium–potassium alloy. The line leading to the above reservoirs and pump is then sealed off and the tube shaken for twelve hours. The two reactions

$$\begin{aligned} \mathrm{Na} + \mathrm{RCl} &= \mathrm{R} + \mathrm{NaCl} \\ \mathrm{Na} + \mathrm{R} &= \mathrm{Na}^{+} + \mathrm{R}^{-} \end{aligned} \tag{7}$$

may be followed by the color change, first to yellow and then to red. The reaction appears to be complete in less than five minutes. However, the solution is clearer if the shaking is continued for several hours. Tilting the tube and cooling Tube A with ice filters the ether solution through the alundum disk sealed in at C. Distillation of the ether back onto the sodium amalgam twice serves to rinse over 99% of the sodium-triphenylmethyl. The tubes are then sealed off at D and mercury run into Tube A through the stopcock which had been previously filled with a little mercury. Tube A is then placed inside of a small thermostat which keeps the tube entirely dark and the whole apparatus is shaken on a special shaker[4] for twelve hours. Tube A is then attached by rubber connections to a receiving flask for analysis, the flask evacuated and the ether vapor allowed to force the dilute amalgam into the flask, the process being carried out with the tube still in the thermostat and the mercury coming in contact with none of the rubber connections. The dilute amalgam is then boiled with standard 0.01 M sulfuric acid, in contact with platinum to cut down overvoltage, and the amount of sodium is obtained by titration. The mercury is also weighed and the volume of ether obtained by weighing an equal volume of water.

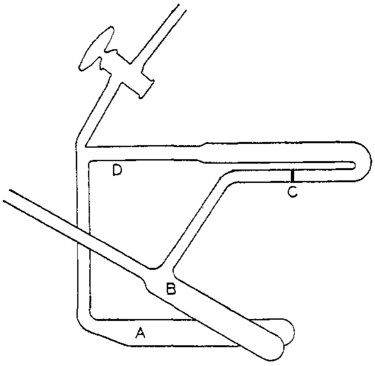

Fig. 1.

Materials

The triphenylchloromethane was prepared from recrystallized carbinol by treating with dry hydrogen chloride in dry benzene in the presence of calcium chloride and was recrystallized until the melting point was above 110°. Analysis for chlorine by the Volhard method gave a value which indicated that the material was over 99.9% pure. The compound was kept in the dark in a special bottle provided with a mercury seal and containing a little calcium chloride. Samples could be obtained from this bottle without introducing any air. The final set of experiments used in the calculations was carried out over a period of about a month and the compound again analyzed at the conclusion, giving 99.1% of the calculated amount of chlorine.

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[4] Bent, *Ind. Eng. Chem., Analytical Edition*, **2**, 106 (1930).

The ether was stored over sodium–potassium alloy and not used until after the alloy had stopped reacting and remained perfectly bright. It was found possible to use a good grade of rubber stopcock grease on the stopcock of this storage flask provided it was maintained a few degrees above the temperature of the room by a small incandescent bulb placed near it which prevented the ether vapor condensing in the grease.

The sodium was melted and run through a constriction to remove dross and previously washed mercury distilled onto it.

Blank determinations failed to show any correction for impurities in the mercury or sodium or amalgam carried over with ether into the second tube.

Calculation of Results

The experimental data give the weight of triphenylchloromethane, the weight of mercury, the number of gram atoms of sodium removed by the mercury and the volume of ether. Since the sodium amalgam used to convert the chloride into the sodium salt is relatively very concentrated (amalgam in equilibrium with solid amalgam), all of the chloride is converted into the sodium salt during the first shaking. The number of gram atoms of sodium removed by the mercury is, therefore, equal to the number of moles of free radical in dilute solution. Subtracting this from the number of moles of chloride introduced at the beginning of the experiment gives the number of moles of triphenylmethyl ion and of sodium ion. These data together with the volume of ether and weight of mercury give all that is necessary for calculation of the equilibrium constant of Equation 2.

In more concentrated solutions the number of gram atoms of sodium removed by the mercury gives not the number of moles of the free radical (R) but $R + 2R^2/nK_1$ in which K_1 is the equilibrium constant of Equation 1 and n is the number of moles of ether. In the same way the total amount of sodium left in solution gives $R^- + (R^-)^2/nK_3$ in which R^- is the number of moles of triphenylmethyl ion. Values for the equilibrium constants of Equations 1 and 3 were obtained by successive approximations and the results are given in Table I. Unfortunately it is not possible to show by any simple graphical method the determination of these constants, due to the number of constants involved and the analytical necessity of removing as nearly as possible half of the sodium.

The first column gives the number of the run. The second gives the number of gram atoms of sodium removed by the mercury. Subtracting this from the number of moles of triphenylchloromethane gives the number of moles of sodium ion plus any un-ionized salt. The fourth and fifth columns give the number of moles of ether and mercury while the last two give the logarithm of the equilibrium constant of Equation 2. The values obtained in the next to the last column are simply a result of assuming, as a first approximation, no association. A large number of such approximations indicate the values given in the last column to be the most probable with an uncertainty of a power of ten in K_1 and K_3. That the uncertainty in these constants is so large is due first to the fact that the activity of an

TABLE I

VALUES OF EQUILIBRIUM CONSTANTS

Run	G. atoms of Na removed $\times 10^4$	G. atoms of Na left $\times 10^4$	Moles of ether	G. atoms of Hg	Log K_2	
					$K_1 = \infty$ $K_3 = \infty$	$K_1 = 10^{-4}$ $K_3 = 10^{-4}$
41	0.393	0.432	0.171	0.875	13.68	13.41
46	0.960	0.474	.121	0.883	13.13	12.99
42	1.340	0.481	.122	1.103	12.96	12.87
43	2.282	1.358	.109	1.063	13.40	13.01
44	4.005	3.775	.117	1.013	13.77	13.14
32	1.55	0.755	.061	0.967	13.47	13.13
33	1.43	0.925	.074	1.020	13.65	13.24
34	1.34	0.880	.076	0.908	13.60	13.23
35	1.40	0.790	.079	1.025	13.51	13.18
36	3.45	2.78	.047	0.952	14.01	13.29
37	0.308	0.208	.095	1.083	13.87	13.44
38	0.265	0.352	.168	0.735	13.77	13.52

Runs 39 and 40 were made in very dilute solutions and for this reason involved such large percentage errors as to be of no value. Run 45 showed precipitation, probably of peroxide as a result of a small leak, and was, therefore, also discarded.

ion is not exactly equal to its concentration in even these dilute solutions.[5] In the second place, the amalgams are very dilute, thus introducing a rather large error from the analysis. Finally, very accurate data are necessary in order to determine three constants with any precision. Fortunately there are other means, which are described below, of determining these two constants which confirm the above values.

The first five runs given in the table are considered to be the most reliable. Runs 32 to 35 were carried out at one concentration in order to determine the reproducibility of the results at that concentration, and Runs 37 and 38 for the same reason at a lower concentration; 13.1 is taken as the value of log K_2, the probable error being less than 0.1. However, a variation of K_1 or K_3 by a power of ten affects log K_2 by about 0.5, so that this should be taken as a measure of the accuracy of this figure.

Since $\Delta F = -RT \ln K$ we find the free energy change for Reaction 1 to be +5.5 kilogram calories, (2) −17.9, (3) +5.5, (4) −23.4, (5) −30.3 and (6) −40.3.

K_1 has been determined by Ziegler and Ewald[6] in a variety of solvents and at 25°. Expressing concentrations as mole fraction, K_1 is found to vary from 0.1×10^{-4} to 1.5×10^{-4}, the value 0.5×10^{-4} being very close to that given in many solvents. Unfortunately no measurements were made on ether solutions, but the value is probably not far from 0.5×10^{-4}. This is well within the limit assigned to the probable error of K_1 above.

K_3 cannot be checked so well. Schlenk and Marcus[7] have found the

[5] Kraus and Bray, THIS JOURNAL, **35**, 1353 (1913).

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

[7] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

equivalent conductance of sodium-triphenylmethyl in ether to be 4.8×10^{-2} for a solution containing 0.4 g. of salt in 40 cc. of ether. This measurement does not permit calculation of the degree of dissociation inasmuch as Λ_∞ is unknown. However, the conductivity is so small as to indicate no large dissociation.

The value of the electron affinity of the free radical in the gaseous state is obtained by adding the following equations

			ΔF	
$^1/_2$ ($R_{2\text{ether}} + 2\ Na_{\text{solid}}$	$= 2Na^+_{\text{ether}} + 2R^-_{\text{ether}}$)		-15.15	(2)
$Na^+_{\text{ether soln.}}$	$= Na^+_{\text{gas}}$		$+79.9$	(8)
$R^-_{\text{ether soln.}}$	$= R^-_{\text{gas}}$		$+27.3$	(9)
Na_{gas}	$= Na_{\text{solid}}$		-18.5	(10)
$^1/_2$ ($R_{2\text{gas}}$	$= R_{2\text{liquid}}$)		$-\ 4.3$	(11)
$R^-_{N=1}$	$= R^-_{N=0.0043}$		$-\ 3.24$	(12)
$Na^+_{N=1}$	$= Na^+_{N=0.0043}$		$-\ 3.24$	(13)
$^1/_2$ ($2R_{\text{gas}}$	$= R_{2\text{gas}}$)		$-\ 4.0$	(14)
$Na_{\text{gas}} + R_{\text{gas}}$	$= Na^+_{\text{gas}} + R^-_{\text{gas}}$	$\Delta H = \Delta F =$	$+58.87$	(15)
$Na^+_{\text{gas}} + \ominus$	$= Na_{\text{gas}}$	ΔH	-118.0	(16)
$R_{\text{gas}} + \ominus$	$= R^-_{\text{gas}}$	ΔH	-59.0	(17)

The values for ΔF and ΔH are given in kilogram calories. Values for Equations 8 and 9 are calculated by the method of Born,[8] and are thought to be good to perhaps three kg. cal. for the sodium ion and one kg. cal. for the triphenylmethyl ion. The fact that the dielectric constant is small for ether as compared with water would seem to justify one in expecting the results to be at least as good as in aqueous solution. The radius of the sodium ion is that used by Born for aqueous solutions, while the value for the triphenylmethyl ion is calculated from the molecular volume of triphenylmethane. The difference between the volume of this compound and the ion has been considered to be due to the loss of one hydrogen, calculated by Kopp's law and the addition of one electron. Born[8] has determined the magnitude of the change in volume resulting from the addition of an electron to a number of atoms. Unless the effect on triphenylmethyl is of an entirely different order of magnitude, the mean of these values may be used without introducing any significant error. The value for Equation 10 is calculated from the vapor pressure of sodium at 25°. ΔF for Reactions 11 to 14 is so small that a very rough estimate is all that is necessary. The vapor pressure of hexaphenylethane has been calculated for Reaction 11 by taking the boiling point as 450° and applying Trouton's rule. The assumption that the activity of hexaphenylethane in ether is equal to the mole fraction for supercooled hexaphenylethane introduces an error which is probably less than 0.5 kilogram calorie.[9] Reactions 12 and 13 are necessary in order that the concentration in the gaseous state may be one atmosphere, a mole fraction of 0.0043 in ether giving a concentration of one mole in a molar volume. The value for Reaction 14

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[8] Born, *Z. Physik*, **1**, 45 (1920).

[9] Hildebrand, "Solubility," The Chemical Catalog Co., New York, **1924**, p. 156.

is obtained by taking the value in ether solution and correcting for the change in activity in passing to the gaseous state. Several assumptions were made and checked on nitrogen dioxide and formic acid. Inasmuch as an effort is being made to measure this reaction in the gaseous state and also the vapor pressure of hexaphenylethane, it is perhaps unnecessary to discuss the method further. Reaction 15, which is the sum of the above eight equations, gives the free energy change for concentrations of one atmosphere. However, since there is no change in entropy for such a gaseous reaction, the various species on both sides of the reaction having the same weight, this value may also be taken as ΔH for the reaction. Combining with Reaction 16 then gives the electron affinity of the free radical as 59 kilogram calories with a probable error of about five kilogram calories. The error in ΔF for Equation 8 is thought to be less than three kilogram calories and for all of the other reactions less than one kilogram calorie.

The author takes pleasure in expressing his appreciation of the interest and suggestions of Dr. W. H. Carothers.

Summary

The addition of sodium to triphenylmethyl has been found to be a reversible reaction. ΔF for this reaction has been determined and also for the dissociation of hexaphenylethane and sodium-triphenylmethyl. The electron affinity of triphenylmethyl in the gaseous state has been found to be 59 ± 5 kilogram calories.

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[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF BRISTOL]

THE ACTION OF DIAZOMETHANE ON SOME AROMATIC ACYL CHLORIDES. V. THE MECHANISM OF THE REACTION

BY T. MALKIN AND M. NIERENSTEIN

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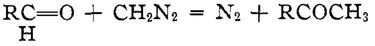
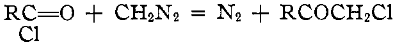
In Part III of this series[1] an attempt was made to coördinate the Schlotterbeck reaction[2] with what has now become known as the Nierenstein



$$\underset{H}{RC}{=}O + CH_2N_2 = N_2 + RCOCH_3$$

reaction.[3] It was suggested that the two reactions, where X = H (Schlot-



$$\underset{Cl}{RC}{=}O + CH_2N_2 = N_2 + RCOCH_2Cl$$

terbeck) and X = Cl or Br (Nierenstein) proceed as follows

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[1] Lewis, Nierenstein and Rich, THIS JOURNAL, **47**, 1728 (1925).

[2] Schlotterbeck, *Ber.*, **40**, 479 (1907).

[3] (a) Clibbens and Nierenstein, *J. Chem. Soc.*, **107**, 1481 (1915); (b) Nierenstein, *ibid.*, **117**, 1153 (1920); (c) Nierenstein, Wang and Warr, THIS JOURNAL, **46**, 2554 (1924); (d) Kahil and Nierenstein, *ibid.*, **46**, 2557 (1924); (e) Lewis, Nierenstein and Rich, *ibid.*, **47**, 1728 (1925); (f) Dale and Nierenstein, *Ber.*, **60**, 1026 (1927); (g) Malkin and Nierenstein, *ibid.*, **61**, 797 (1928).