

with those obtained by the method described previously. It is felt that the use of this apparatus offers a rapid as well as a very accurate means for determining partial vapor pressures of binary mixtures.

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THE ELECTRON AFFINITY OF FREE RADICALS. III. FURTHER STUDIES OF FREE RADICALS CONTAINING BIPHENYL AND NAPHTHYL GROUPS

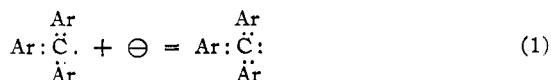
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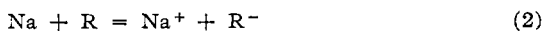
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The addition of an alkali metal to an unsaturated compound is a type of reaction which is peculiarly adapted for study in connection with the problem of finding the effect on the strength of a given bond of various substitutions in a molecule. Heats of combustion and dissociation constants of acids give similar data but have their own peculiar limitations. Heats of combustion are commonly so large as to mask very largely changes in a single bond. Ionization data for acids are difficult to obtain in solvents which have a stronger affinity for the proton than the base from which the acid is derived. The addition of alkali metals to unsaturated compounds supplies a very wide range of reactions to be studied and reactions which are at least in some cases reversible.

Not only will sodium add to such unsaturated single bond compounds as organic free radicals but it will also add to some double bond compounds such as ketones and olefinic compounds and to apparently saturated molecules such as triphenyl boron and triphenyl aluminum. The variety of reactions which may be studied is, therefore, all that can be desired providing equilibrium measurements are possible. It has been shown¹ that the sodium may be removed from the free radical addition compounds with the aid of mercury and that by knowing the concentration of the amalgam which is in equilibrium with the free radical and the addition compound, the free energy for the addition of sodium to the free radical may be calculated (Equation 2). A comparison of various free radicals, since in every case sodium ion is formed, is, therefore, a comparison of the reaction



of formation of the negative ion from the free radical (Equation 1). The equilibrium studied experimentally is



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

In these equations Ar represents any aromatic group while R represents the whole free radical, such as triphenylmethyl.

It has been found that the free energy changes for reaction (2) and, therefore, also for reaction (1) in the case of four free radicals, do not differ by more than 2 kg. cal. Therefore, the addition of an electron to an "odd" molecule to complete the group of eight electrons about the central carbon, or in other words the addition of an electron to an unshared electron to form an electron pair involves an energy change which is practically independent of the substituents on the atom involved. This fact is of particular interest inasmuch as a pair of similar electrons forms the non-polar bond in the corresponding ethanes. That the energy here measured should be the same for a variety of compounds is additional evidence that the electron pair, as first suggested by G. N. Lewis, acts as a unit in the formation of non-polar bonds.

A close examination of the data reported in the second paper of this series² brought out the fact that the variations in the electron affinity which are less than 2 kg. cal. are quite regular, larger molecules having the stronger affinity. This observation coupled with the observation that it is the larger of these free radicals which shows the smallest tendency to associate forming the ethane led to the hypothesis that the weakness of the bond which leads to the formation of the ethane is due not to the force between two carbons being less but to the fact that the force has operated through a smaller distance, due to the steric hindrance of the large phenyl groups, and, therefore, the resulting energy of binding is much less.

These deductions have been based on the study of but four compounds. This number being so small, it would seem very desirable to study a larger number of compounds of the same type in order to verify or delimit these tentative conclusions. This paper describes work on four more compounds which may be described as triphenylmethyl in which biphenyl or naphthyl has replaced one or more phenyl groups. These compounds are all of the same type as those heretofore studied in that they contain only aromatic hydrocarbon substituents. The results are entirely in accord with those previously reported. The ease of removing sodium from the addition compound is about the same for all of the compounds studied, the larger free radicals having a slightly greater affinity for the sodium, and, therefore, a slightly greater electron affinity. The effect of the various groups is nearly additive, so that it is possible to predict with considerable accuracy a value for the equilibrium constant of the reaction.

Procedure

The experimental procedure has been modified somewhat with the result that the data are considerably more accurate. The method of making the amalgams and intro-

² H. E. Bent, *THIS JOURNAL*, 53, 1786 (1931).

ducing them into the evacuated system has been developed to a point where it now seems quite satisfactory and not very laborious. Figure 1 shows the flask used in preparing the amalgams. Sodium is first dried from oil with filter paper, surface oxide removed as shavings, and introduced into the straight tube above the flask. A glass weight above the sodium helps to break the oxide shell, which otherwise retards the flow of liquid metal. The tube is then sealed off as shown and the whole system evacuated. With the mercury pump still in operation the sodium is gently warmed. This gives time for reaction of the metal with any hydroxide which may have been formed during the brief time required for sealing the tube. Finally, the temperature is raised to the melting point, the molten sodium running through the constriction and giving a perfectly clean surface. Mercury is then distilled from the small flask with the aid of a small flame from a Bunsen burner. The apparatus is evacuated during the whole distillation, which may be carried out in a few hours with practically no supervision. Early in the process, after about three equivalents of mercury have been added, the amalgam is heated to the melting point in order to insure complete solution of the rather infusible compounds. Thereafter the latent heat of condensation maintains the temperature above the melting point of the amalgam. When it is estimated that the composition is near that of the saturated amalgam, about five atom per cent., the flask is allowed to cool to room temperature. If the amount of solid phase is too large, further mercury may be introduced into the small flask through the stopcock and the distillation continued until there is but a small amount of solid phase. The flask is then sealed

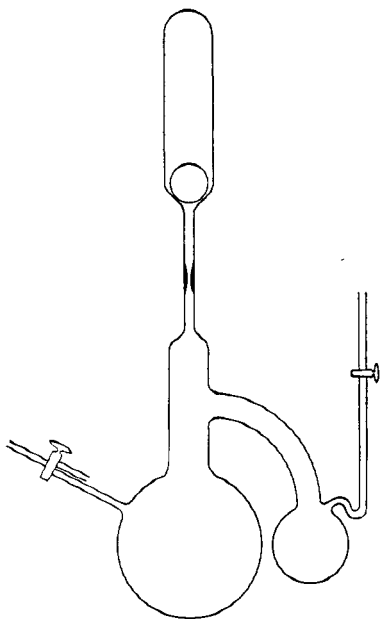


Fig. 1.—Apparatus for preparing amalgam.

to another flask by means of the three way stopcock, this latter flask evacuated, the pump sealed off and then by tipping the saturated amalgam is poured into the second flask. Slight warming before pouring ensures an amalgam which will be saturated when cooled.

The flask containing the saturated amalgam is then inverted, the stopcock passing through a ring padded with cloth, and sealed to a second stopcock, Fig. 2. This has been found to be necessary due to the fact that prolonged contact of amalgam with stopcock grease gradually spoils the grease in a band around the plug passing over the two ends of the bore. The upper stopcock, therefore, serves merely to hold the amalgam, the lower one serving to hold the vacuum. The lower one is, of course, opened before any amalgam is taken from the flask. The ether is kept in the lower flask, stored over sodium-potassium alloy as described in the first paper of this series. It has been found possible to keep the stopcock of this flask in good condition by maintaining it a few degrees above room temperature. After perhaps twenty to thirty samples have been removed, it sometimes becomes necessary to regrease this cock. This may be done without admitting air to the flask by first warming the flask with a beaker of water to a temperature five to ten degrees above the boiling point of ether. The plug is then removed, and old grease is wiped clean while ether is slowly distilling out of the flask. Before regreasing, the plug is heated considerably above the temperature of the bath by im-

mersing it in a beaker of boiling carbon tetrachloride. On inserting the hot regreased plug very little ether condenses in the grease. The flask is then rapidly cooled by ice water before the plug has time to cool below the temperature of the ether. The tube surrounding the lead to the apparatus is filled with ice and water when it is desired to introduce ether, the mercury pump being cut off by the cock in the pump line.

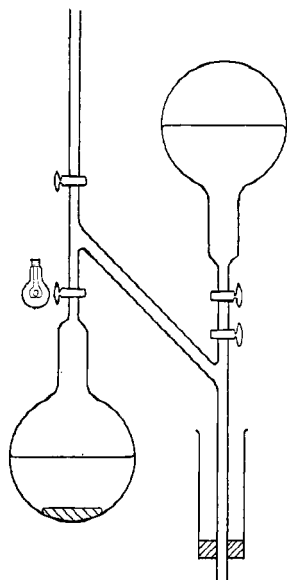


Fig. 2.—Storage flasks for ether and amalgam.

Two changes in manipulation have been made which considerably improve the reliability of the data. Heretofore it has always been noticed that a small amount of liquid is decolorized when filtered and transferred to the second tube of the apparatus³ for treatment with mercury. The amount has been so small, about 5%, as not to affect the results seriously, but has been a continued source of uncertainty. This has been practically eliminated by freezing the ether solution in liquid air before sealing off from the pump line or sealing between the two tubes. Apparently there is sufficient decomposition of ether at the temperature of Pyrex glass during the sealing to liberate an appreciable amount of water. A second improvement in technique has been to rinse the apparatus with ether vapor before introducing the bulk of the ether. It is not possible to bake out the Pyrex thoroughly before each run due to the fact that the sample of chloride is placed in the tube before attaching to the pump for evacuation. The small amount of oxygen or water which is so tenaciously held by the glass can apparently be removed by displacing it with ether. The procedure is to admit a little ether to the apparatus after a preliminary evacuation, and then to pump down again to about 10^{-4} mm. of mercury pressure. Presumably the ether is adsorbed on the glass more strongly than the water, and, therefore, cleans up the surface. It may be that Ziegler's⁴ success in cleaning up the glass in his experiments on hexaphenylethane in very dilute solution was due rather to the solvent used than to the free radical dissolved in it.

Materials

The authors are greatly indebted to Dr. W. F. Bruce, who prepared the carbinols from which our free radicals were derived. In every case the carbinol was converted into the corresponding chloride with the aid of hydrogen chloride gas. Inasmuch as some difficulties were encountered in the preparation some detail as to the procedure will be given. The most difficult part of the problem seemed to be to obtain the chlorides of such purity that a Carius analysis would give at least 97% of the calculated amount of chlorine. Since the chief impurity was carbinol, formed by hydrolysis, this gave an excellent check on the purity of the compound. In some cases there were highly colored impurities which crystallized separately from the chloride but had solubilities so nearly the same as the chloride as to make separation difficult.

³ Tube A, Fig. 1, Reference 1.

⁴ Ziegler and Ewald, *Ann.*, **473**, 183 (1919).

β -Naphthylidiphenylchloromethane.—The carbinol was prepared according to the directions in the literature,⁵ dissolved in ethyl ether and converted into the chloride by treating with dry hydrogen chloride gas. In order to avoid the difficulties with tarry impurities reported by Gomberg and Sullivan, which required treatment with bone black and recrystallization, we tried using freshly distilled ether, hoping that the absence of peroxide would give a cleaner product. This proved to be the case, fine white crystals being obtained without the necessity of using bone black. It is especially desirable to avoid the use of bone black on account of the hydrolysis of the chloride which is certain to take place unless great precautions are taken to have the bone black free from adsorbed moisture. The chloride was recrystallized three times by adding petroleum ether to the ethyl ether solution and cooling to 0°. The final product melted at 95°. The previously reported melting point is 94.5°.

Anal. Calcd. for $C_{22}H_{17}Cl$: Cl, 10.79. Found: Cl, 10.73, 10.75.

Phenylidibiphenylchloromethane.—The carbinol was prepared according to the directions of Schlenk.⁶ Considerable difficulty was encountered, however, in attempting to obtain the carbinol from the benzene solution in which it was prepared, only tars or oils being obtained. The attempt was then made to treat the benzene solution with hydrogen chloride and crystallize the chloride. Here also the attempts to crystallize the chloride from benzene, ether, petroleum ether, ligroin and various mixtures of these resulted in nothing but oils. The treatment with hydrogen chloride produced an intense red color and a small amount of red crystalline material separated but apparently none of the desired chloride. The difficulties encountered were undoubtedly due to the fact that the carbinol was too impure to start with. However, attempts to purify the solution by treating it with bone black, or by steam distillation of the oily carbinol obtained by precipitation, while undoubtedly removing some impurities, did not suffice to give crystalline material. Finally it was found that fractional precipitation of tarry materials by means of petroleum ether, gave material which became continually lighter in color and more crystalline until the last half was almost white; 5 g. of this material was dissolved in 75 cc. of benzene. Treatment with calcium chloride and dry hydrogen chloride again gave a bright red solution and on adding 50 cc. of petroleum ether and cooling to 0°, about 0.4 g. of red crystals formed, leaving the mother liquor much lighter in color. The liquid was decanted from these crystals, evaporated to 20 cc., 30 cc. of petroleum ether added and the solution again allowed to stand at 0°. Crystals with but a slight pink tinge formed from this solution; these were crystallized four times more from benzene and petroleum ether. The final product weighed 1.4 g. and melted at 132°. The melting point previously reported is 131.5°.

Anal. Calcd. for $C_{30}H_{25}Cl$: Cl, 8.25. Found: Cl, 8.01, 8.24.

α -Naphthylidibiphenylchloromethane.—The carbinol prepared by the method of Schlenk and Bornhardt⁷ and recrystallized from xylene melted from 211–214°, while their material melted at 228°. We, therefore, extracted the carbinol from excess dibiphenyl ketone with ether, using a continuous extraction apparatus, and thereby obtained material melting from 225–227°. Six grams of this material was then dissolved in 175 cc. of benzene, calcium chloride added and the solution treated with hydrogen chloride. A small amount of white solid precipitated and was discarded, while the solution became intensely blue in color. This color was largely removed by treatment with bone black, leaving a light orange colored liquid. The bone black was carefully dried before use in order to prevent hydrolysis of the chloride, by evaporating to dryness three

⁵ Gomberg and Sullivan, *THIS JOURNAL*, **44**, 1813 (1922).

⁶ Schlenk, *Ann.*, **368**, 300 (1909).

⁷ Schlenk and Bornhardt, *Ber.*, **46**, 1482 (1913).

times from benzene and finally heating to red heat and cooling in a desiccator; 175 cc. of petroleum ether was added to the benzene solution of the chloride and the solution cooled to 0°. About 0.5 g. of a blue solid separated and was discarded. The mother liquor was evaporated to 50 cc., 50 cc. of petroleum ether added and the solution allowed to stand at room temperature. A white solid with orange crystals separated. Recrystallization twice from benzene and petroleum ether gave a final product which weighed one gram, was composed of small white needles and melted at 215–216°. The melting point previously reported is 214–216°.

Anal. Calcd. for $C_{35}H_{25}Cl$: Cl, 7.38. Found: Cl, 7.14, 7.20.

Tribiphenylchloromethane.—The procedure for preparing this compound differed somewhat from that described in the literature.⁸ Two grams of magnesium powder activated by Baeyer's method⁹ was added in three nearly equal portions to a solution of 15 g. of dry *p*-bromobiphenyl¹⁰ in 25 cc. of dry ether. A vigorous reaction took place. After the solution had been refluxed for three hours, 25 cc. of benzene was added and 15 g. of dibiphenyl ketone in four portions. The solution of the ketone occurred rapidly with evolution of considerable heat and the production of a green color which later became purple. The material was refluxed for four hours and the magnesium derivative then obtained in solid form by the addition of petroleum ether. This material was rubbed with ammonium chloride solution in a mortar and recrystallized from benzene. The melting point of the product was 196–199°. After extraction with ethyl ether to separate the product from any unchanged ketone the melting point was 205–207°. The previously recorded value is 208°. Five grams of this carbinol was treated with dry hydrogen chloride gas in the presence of a little calcium chloride. The solution became dark purple in color and retained this color after boiling down to 50 cc. After standing at room temperature a solid precipitated, leaving the mother liquor yellow in color. After decantation an equal volume of petroleum ether was added and the solution allowed to stand at 0°. Small white crystals formed together with a small amount of an intensely colored purple solid. Upon warming with benzene, however, the white crystals dissolved first so that it was possible to obtain a separation by rapid decantation at the proper point. Three more crystallizations from benzene and petroleum ether gave one gram of white material melting at 198°. The recorded value in the literature is 195°.

Anal. Calcd. for $C_{37}H_{27}Cl$: Cl, 7.00. Found: Cl, 6.84, 6.80.

Experimental Results

Table I gives the experimental data for the equilibrium measurements. These were obtained over as large a range of concentration as the solubility of the compounds and the analytical procedure would permit. The three columns headed $\log K_2$ give values of the equilibrium constant for equation (2). The column headed $K_3 = \infty$ is included in order to show the magnitude of the change in the equilibrium constant which would be produced by assuming complete dissociation of the sodium addition compound into sodium ion and a free radical ion with one negative charge. These compounds undoubtedly are not completely dissociated and, therefore, a value

⁸ Schlenk and Weickel, *Ann.*, **372**, 1 (1910); Schmidlin, *Ber.*, **45**, 171 (1912); Schlenk, *ibid.*, **46**, 1475 (1913); Schmidlin, "Das Triphenylmethyl," p. 169.

⁹ Houben-Weyl, Vol. IV, 1924, 724.

¹⁰ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 42.

for this dissociation constant of 10^{-4} has been assumed for all of these compounds.¹ A variation of one power of ten in this constant changes the value of $\log K_2$ by about 0.5. A second dissociation which must be considered is that of the ethane into the free radical. The particular compounds chosen for this study were selected on account of the fact that the ethanes are so nearly completely dissociated into the free radicals at the concentrations at which we are working that we may assume complete dissociation. In the case of the last compound in the table, however, this assumption is not justified. The value for the dissociation constant for this ethane has been taken as 10^{-3} , based on the fact that molecular weight determinations in naphthalene indicate this compound to have a constant ten times as large as hexaphenylethane.¹¹ The value for hexaphenylethane used in the first paper of this series was 10^{-4} . All values for these constants are here calculated with concentrations expressed as mole fractions. Since all of the other free radicals have been shown by molecular weight determinations to be more dissociated than β -naphthylidiphenylmethyl, it is legitimate to assume complete dissociation in the calculations.

The relation between the total amount of compound in solution and the amount which is dissociated may be derived in the following manner: let R be the number of moles of free radical, R_2 the number of moles of ethane, n the number of moles of solvent, K the equilibrium constant for the reaction

$$R_2 = 2R$$

and a be the amount of free radical determined analytically (that is, $R + 2R_2$). We then have the equations

$$\begin{aligned} a &= R + 2R_2 \\ K &= \frac{(R/n)^2}{R_2/n} = \frac{R^2}{nR_2} \end{aligned}$$

Eliminating R_2 gives a quadratic equation in R

$$R = \frac{-1 + \sqrt{1 + 8a/nK}}{4/nK}$$

only the positive value of the root being significant. This may be expanded by the binomial theorem giving

$$R = a - 2a^2/nK + 8a^3/n^2K^2 \dots$$

Therefore

$$R/a = \alpha = 1 - 2a/nK + 8a^2/n^2K^2 \dots$$

when α is fraction dissociated. Hence when $a = 1/10nK$, the error in assuming complete dissociation is less than 15%, and if K is larger by a factor of 10, the error is about 2%.

Making use of the relation $\Delta F = -RT \ln K$ we may convert these values

¹¹ P. Walden, "Chemie der freien Radikale," S. Hirzel, Leipzig, 1924.

of the equilibrium constants into free energy values as shown in the last column of the table.

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	$\overbrace{K_3 = \infty}^{\text{Log } K_2}$ $\overbrace{K_3 = 10^{-4}}$ Mean			$-\Delta F$
Phenyldi- phenyl- methyl	0.125	0.407	0.152	3.92	15.33	14.54		
	.150	.586	.162	4.87	15.55	14.76		
	.201	.932	.181	2.57	15.37	14.47		
	.487	1.673	.151	4.72	15.46	14.28		
	.627	2.983	.165	4.80	15.61	14.35	14.48	19.8
Tribiphenyl- methyl	.085	0.785	.151	3.96	16.24	15.33		
	.118	.614	.144	4.77	15.84	15.00		
	.198	1.217	.139	4.97	16.02	14.93		
	.211	1.709	.142	5.05	16.26	15.05		
	.266	1.994	.182	5.01	16.08	14.90	15.04	20.6
α -Naphthyl- dibiphenyl- methyl	.0081	0.245	.158	4.81	15.34	14.81		
	.0225	1.075	.190	4.92	15.66	14.73		
	.105	0.378	.165	4.92	15.48	14.83		
	.211	.835	.171	5.55	15.60	14.71		
	.307	1.969	.181	4.71	15.92	14.75	14.77	20.2
β -Naphthyl- diphenyl- methyl	.246	0.466	.121	2.81		14.14		
	.269	.443	.164	3.22		14.03		
	.718	1.081	.156	2.96		13.72		
	1.307	1.079	.105	3.27		13.55		
	1.526	1.557	.138	3.31		13.44	13.78	18.6

These values are for the reaction of addition of sodium to free radical to form the positive sodium ion and the negative free radical ion. The standard state for the sodium is taken as the metal and for the other materials the activity is taken as equal to the mole fraction.

These free energy values together with those previously obtained have been expressed graphically in Fig. 3, in which the free energy is plotted as ordinate and the number of benzene rings in the molecule as the abscissa. The upper curve is the biphenyl series, starting with triphenylmethyl and passing to the compounds which contain one, two and three biphenyl groups. The lower curve has also been drawn through the point for triphenylmethyl and might be called the naphthyl curve, since there is one naphthyl group in the rest of the compounds. The point on this curve at 18.6 kg. cal. represents both α -naphthyldiphenylmethyl and β -naphthyldiphenylmethyl, both of these compounds giving the same value. The last two compounds contain one and two biphenyl groups, respectively, in addition to the α -naphthyl group. These curves substantiate the conclusions of the previous paper of this series. In the first place the values of the free energy change for the reactions all fall within the rather narrow range of 2.5 kg. cal. In the second place, the effect of replacing phenyl by

naphthyl or biphenyl is nearly additive, the former apparently having a slightly smaller effect than the latter. It would seem probable that a prediction could be made for trinaphthylmethyl of 19.3 ± 0.3 .

It is possible from these data to infer something as to the dissociation constant of the sodium addition compounds. Since there are almost no experimental data on the subject, a value of 10^{-4} has been assumed for all of these compounds.¹ The fact that this assumption gives values of ΔF which differ little from each other, indicates that the assumption is probably correct. It is possible that the dissociation constant changes as we pass from one compound to another, and that these changes are just compensated by some other factor changing in the opposite direction. Since such an assumption is less probable, we may infer that the dissociation constants for these sodium addition compounds are essentially the same. It should be noted, however, that ΔF is not particularly sensitive to changes in the dissociation constant and, therefore, these data indicate only that this constant does not change by many powers of ten.

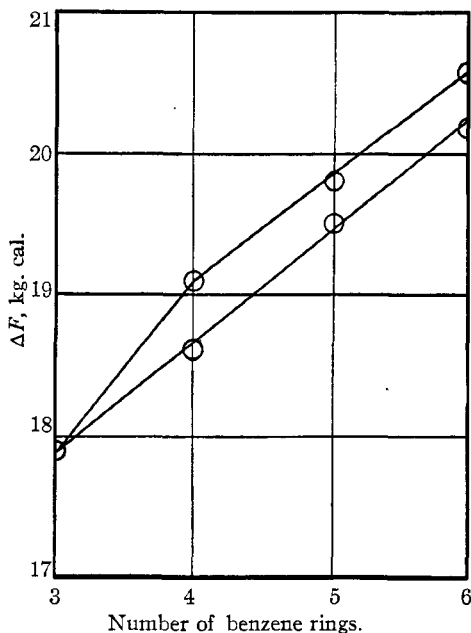


Fig. 3.—The free energy of addition of sodium to free radicals. The upper curve is for the biphenyl series. The compounds represented by the lower curve may be considered as triphenylmethyl in which the first phenyl is replaced by naphthyl and the second and third by biphenyl.

Conclusions

The reaction of addition of sodium to four organic free radicals has been studied quantitatively, these compounds being phenyldibiphenylmethyl, tribiphenylmethyl, α -naphthyldibiphenylmethyl, and β -naphthyldiphenylmethyl.

The conclusions of the second paper of this series have been found to be borne out by this study. These conclusions were, first, that the values for the free energy of addition of sodium to these free radicals all fall within rather narrow limits; second, that within these limits the effects produced by the various groups are additive.

CAMBRIDGE, MASSACHUSETTS