and potassium chlorides are in accord with solubility determinations and, except for a minor discrepancy between the sodium and lithium ions, with the theory in question. Many additional experiments of this type in combination with precision dielectric constant determinations of the kind described here are required before a complete and searching examination can be made of the assumptions introduced for the purpose of quantitative calculations.

It is the intent of this report to show that in the more dilute aqueous salt solutions dielectric constant measurements of the kind described lead to calculated solubilities in good agreement with those actually observed, and to point out that in the case of most systems containing moderate to high concentrations of electrolyte the comparison shows the important effect in the salting-out to be a displacement of non-electrolyte from the electrical field about the ion. The data contribute to the establishment of the fundamental correctness of the point of view that the primary cause for the salting-out is the change of concentration of the non-electrolyte solute with changing distance from the ion caused by the preferential attraction of the medium of higher dielectric constant by the charged ion.

The author wishes to express his gratitude for the helpful advice of J. W. Williams throughout the course of this work.

Summary

Dielectric constant data have been obtained at several temperatures for aqueous solutions of acetone, aniline, ethyl ether, glycerol, glycine, and urea. Density determinations have been made at 25° for the solutions containing acetone, aniline, glycine, and urea.

These data and the Debye theory of the salting-out effect make possible calculations of the limiting slopes of the solubility curves for the non-electrolyte solutes as a function of salt concentration. In this report attention has been confined largely to systems containing aniline and ethyl ether. The dielectric constant measurements are found to lead to calculated solubilities in good agreement with those actually observed in the more dilute salt solutions and when larger differences appear they seem to be due in considerable measure to the fact that the solubility measurements have been made in a salt concentration range too high for the limiting law of the theory.

The data are most successful in that they contribute to the establishment of the essential correctness of the Debye theory which describes the primary salting-out in terms of the relative electrical susceptibility of the non-electrolyte components and the electrical fields of force in the neighborhood of the ions.

# The Electron Affinity of Free Radicals. XII. ΔF of Addition of Sodium to Organic Compounds by the Potentiometric and Analytical Methods

BY NORMAN B. KEEVIL

Two methods have been described for determining ΔF of addition of sodium to an organic compound. In the first the equilibrium constant of the reaction is obtained by a direct analysis of the equilibrium mixture[1] and in the second the e. m. f.[1] of the cell

$$\begin{array}{c|c|c} \text{Na} & \text{NaR} & \text{R}_2, \text{Pt} \\ \text{amalgam} & \text{solution} & \end{array}$$
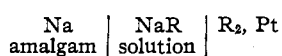
is measured, the two halves of the cell being separated by a sintered Pyrex glass disk.[2]

This paper reports further measurements with free radicals, ketones and unsaturated hydrocarbons, and the results obtained by the two methods are compared. Such data are useful in giving the quantitative effect of different groups on the reaction, thus aiding in the interpretation of structure, and in indicating the relative importance of steric hindrance and resonance energy in determining the properties of the molecule. Also, knowing the ionization potential of sodium, and combining this with suitable equations, the electron affinity of the free radical in the gaseous state may be obtained. This has been done for triphenylmethyl.[3]

(1) IX, Dorfman, THIS JOURNAL, 57, 1455 (1935).
(2) Bent and Keevil, ibid., 58, 1228 (1936).
(3) Bent, ibid., 52, 1498 (1930).

Similar calculations for other free radicals have not been made since the variation in the values of ΔF of addition of sodium in ether solution are within the experimental error of certain values for the equations involved in calculating ΔF for the gas reaction. Although the small differences obtained in ether solution are reproducible and are related to structural differences, the electron affinity has been considered to be constant as a first approximation. An exception to this rule was found in the case of dibiphenylene-diphenylethane.[2] The results obtained with this compound indicated that the unlimited application of the potentiometric method to determine the strength of the C–C bond assuming constant E_0 is not justified. The method may, however, be useful in studying compounds outside of the range accessible analytically, provided data are available for other members of the series. Such a series is the dixanthyl series investigated by Conant[4] and by Bent and Ebers.[5] With the assumption of constant electron affinity for all members of the series one is able to calculate the concentration of free radical and with the assumption of constant entropy change, the heat of dissociation. This is done here for dixanthyl, which previously could be treated only with the aid of many more assumptions.[6]

Purification of Materials.—α,γ-Bis-diphenylene-β-phenylallyl prepared by Dr. C. F. Koelsch[7] is a dark green crystalline compound, completely dissociated into free radicals.

Dixanthyl.—The usual precautions in the preparation of this compound were not necessary since the free radical is largely associated, and does not react with oxygen. It was prepared by the method described by Garvey,[8] reducing an acetone solution of xanthydrol using freshly prepared chromous chloride.

The preparation of the other materials has been described in the previous papers of this series.

α,γ-Bis-diphenylene-β-phenylallyl.—This compound reacts with very dilute amalgam, adding one atom of so-

dium per molecule, forming an indigo blue compound.

(4) Conant and Garvey, THIS JOURNAL, **49**, 2599 (1927).
(5) Bent and Ebers, *ibid.*, **57**, 1242 (1935).
(6) Conant, *J. Chem. Phys.*, **1**, 427 (1933).
(7) C. F. Koelsch, THIS JOURNAL, **54**, 4744 (1932).
(8) Garvey, Thesis, Harvard University.

The reaction was incomplete in a day, so eight days of shaking were allowed for equilibrium to be reached. The results are shown in Table I.

TABLE I

EQUILIBRIUM DATA FOR α,γ-BIS-DIPHENYLENE-β-PHENYL-ALLYL

Direction of approaching equilibrium	Removal of Na	Addition of Na
Moles of Na in Hg	1.21×10^{-6}	9.1×10^{-6}
Moles of Na in ether	5.29×10^{-5}	1.25×10^{-4}
Moles of Hg	2.198	0.749
Volume of ether, cc.	69.0	148.0
Moles of free radical	1.87×10^{-5}	7.55×10^{-5}
Log K	19.3	17.8
$-\Delta F$, kcal.	26.8	24.6

Dibiphenylenediphenylethane.—Equilibrium was attained slowly and was not hastened using 40% amalgam. The first step was the formation of a precipitate of chloride, accompanying the formation of free radical. This was followed by slow reaction with sodium. The tubes were shaken for over four months and the equilibrium approached from both sides. The results are given in Table II.

TABLE II

EQUILIBRIUM DATA FOR PHENYLFLUORYL. Na + R = NaR

Chloride, g.	0.0475	0.0558	0.0491
Moles NaR at equil. $\times$ 10^4	1.63	1.78	1.06
Prepn. with	1% am.	1% am.	0.0006 N Na
Shaken with	Mercury	Mercury	Hg with trace Na
Time shaken	1 day	3.5 days	2 months
Moles Na in Hg	$<10^{-6}$	$<10^{-7}$	$<10^{-6}$
Moles Hg	0.697	1.17	0.096
Log K	>20.9	>23	>20
$-\Delta F$	>28.5	>31	>27

The equilibrium lies beyond the range that can be studied accurately by this method, but the results serve as a rough check on those obtained potentiometrically. The value of E_0 calculated from the above data for the addition of two sodium atoms to the ethane is >1.2 volts, while that from e. m. f. measurements is 1.34 volts.

Dixanthyl.—This compound combined very slowly with sodium. In fact Conant and Garvey[4] report that after shaking for more than four hours with 40% amalgam the amount of sodium which had added was less than 2%. In our experiments two samples of ethereal solutions of the sodium salt were prepared by shaking for four months. The reaction appeared to go to completion. The strength of the C–C bond is so great in this compound as to make it

TABLE III

E. M. F. DATA FOR DIXANTHYL

Mole fraction of NaR $\times$ 10^4	5.8	5.28
Mole fraction of R_2 in satd. soln. $\times$ 10^3	1.08	1.08
Activity of sodium	1	1
E. m. f. measd., volt.	0.61	0.611
E_0 for addn. to ethane	.59	.593
Mole fraction of free radical $\times$ 10^9	7.7	7.1
Spurious { Max. value	0.74	1.08
e. m. f. { Last. val. before meas.	.47	0.58

impossible to study its reaction with dilute amalgam. The equilibrium would be so far to one side that a determination of the equilibrium constant would be impossible. The results of e. m. f. measurements are shown in Table III.

From these data we can calculate the dissociation constant for dixanthyl although this constant is so small as to give this compound very few of the characteristics of a free radical. If we follow the procedure of calculating a value for E_0 for the reaction[9] Na + R = NaR from the equilibrium data for other compounds of the same series,[1] we arrive at the value for phenylxanthyl of 0.97, for α-naphthylxanthyl of 0.96 and for isopropylxanthyl 0.84. Since this last value was rather difficult to obtain and is less accurate than the other two we will choose a value for E_0 of 0.90. This gives a concentration of free radical of 7.4×10^{-9} and an equilibrium constant for the process of dissociation of 5.0×10^{-14}. ΔF is then 18.2 kcal. and if we assume ΔH to be greater by 5 kcal. as has been done by Conant we arrive at a value for ΔH of 23.2 kcal. This is considerably lower than the value obtained by Conant, 30.7 kcal. If we assume his value to be correct we would have to choose a value for E_0 in our calculations of 1.06, which seems very improbable. Since the number of approximations required to give the value 30.7 is greater than in the above calculation we will use the value 23.2 in comparing the influence of various substituents on the C–C bond. The following table gives the effect of various substituents on the strength of the C–C bond first as estimated

TABLE IV

EFFECT OF SUBSTITUENTS ON THE C–C LINKAGE

Subst. R	Change in ΔH_{298} of dissociation of ethane caused by replacement of one hydrogen atom by a single group	
	Values given by Conant[8]	Values based on 23.2 kcal. for dixanthyl
Methyl, ethyl	− 5	−1.5
n-Butyl[5]	− 6	−4
Isopropyl[5]	−11	−7
Phenyl	−11	−7
Benzyl	− 7	−4
α-Naphthyl	−13	−9
β-Naphthyl	−12	−8
p-Methoxyphenyl	−12	−8

These are of course only rough values but the last column seems more reasonable since it does not attribute so great an effect to the replacement of a hydrogen by a methyl group.

Fluorenone.—This compound was studied potentiometrically in order to test the applicability of the method to ketones and to compare the results with those obtained analytically.[9]

The resistance of the cells was a little greater than usual, due to the low solubility of the sodium compound, but voltages could be read to hundredths of a volt. The fluctuating initial e. m. f. fell off to a low value before breaking the capsules. The results are shown in Table V. The difficulty of precipitate formation was encountered as in the equilibrium measurements and this discouraged further work on ketyls. In this case it appeared to be the insoluble addition compound of fluorenone and the sodium salt. The solution turned dark after the introduction of fluorenone, and after a few hours a mass of dark green crystals covered the bottom of the cell. However an e. m. f. could be measured which was in accord with the results obtained by the equilibrium method.

Tetraphenylethylene.—The potentiometric method seems also to be applicable to the study of unsaturated compounds. Here no difficulty due to precipitation was encountered and the results are in agreement with the prediction based on the equilibrium method.[9] Due to the low solubility of the sodium salt the conductivity was low. The results are given in Table V.

Discussion of Results

The unexpected high value of the free energy of addition of sodium to phenylfluoryl obtained by the e. m. f. method,[2] is close to the limit found by the analytical measurements. This high electron affinity (compared to triphenylmethyl) has been directly related to the strength of the corresponding hydrogen compound as acid.[2,10] This result was the first to illustrate that the electron affinity cannot be considered as constant for all free radicals in determining the concentration of

TABLE V

E. M. F. DATA FOR FLUORENONE AND TETRAPHENYLETHYLENE

Mole fr. of NaR in ether $\times 10^3$	Mole fr. of R in satd. soln.	Mole fr. of Na in Hg $\times 10^2$	E. m. f. measd., v.	E_0 calcd. from E	E_0 from anal. data[9]	Spurious e. m. f. Max. val.	Last value before run
		Sodium Fluorenone					
E_0 calculated from the equation $E = E_0 - \frac{RT}{nF} \ln \frac{(NaR)}{(Na)(R)}$							
2.24	0.105	5.13	0.40	1.087	1.075	0.120	0.066
1.65	.105	5.13	.41	1.09	1.075	.31	.10
		Disodium Tetraphenylethylene					
E_0 calculated from the equation $E = E_0 - \frac{RT}{nF} \ln \frac{(Na_2R)}{(Na)^2(R)}$							
3.66	1.78×10^{-3}	40% am.	0.33	0.31	0.5	0.502	0.23
3.51	1.78×10^{-3}	a Na = 1	.32	.30	.5	…	0

by Conant based on the value 30.7 for dixanthyl and in the last column based on the lower value reported in this paper.

free radical, even as a first approximation. However, the results obtained with dixanthyl indicate

(9) Bent and Keevil, THIS JOURNAL, **58**, 1367 (1936).

(10) Conant and Wheland, ibid., **54**, 1212 (1932).

that this assumption may be applied to series of compounds where one of the more easily dissociated members has been measured.

The e. m. f. data with fluorenone confirm the data previously obtained by equilibrium measurements and further emphasize the fact that the fluoryl group causes a molecule to have a higher electron affinity than would be produced by diphenylmethylene.

The values for tetraphenylethylene are the first quantitative data for this compound, the equilibrium measurements giving only a maximum value. The very low value for this compound is in striking contrast to the values previously obtained for free radicals and ketones.

The results for α-γ-bis-diphenylene-β-phenyl-allyl are perhaps a little surprising in view of the fact that this compound contains two diphenylene groups. One might have expected a very great tendency to add sodium by analogy with phenyl-fluoryl. It may be that the electron affinity is

high for this compound, but that the shape of the molecule prevents a close approach of the sodium ion to the negative charge.

The author wishes to thank Professor Henry E. Bent for suggesting this problem and for offering many valuable suggestions and criticisms.

Summary

1. The potentiometric method has been shown to be applicable to the study of ketones and unsaturated compounds as well as free radicals.

2. The results obtained by the two methods agree within the experimental limits for fluorenone, tetraphenylethylene and dibiphenylene diphenylethane.

3. ΔH of dissociation of dixanthyl is calculated to be 24 kcal.

4. ΔF of addition of sodium to α-γ-bis-diphenylene-β-phenylallyl = 25 kcal.

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Effect of Polar Groups upon Esterification Velocities of Substituted Benzoic Acids

BY ROBERT J. HARTMAN AND ALVIN M. BORDERS[1]

In recent years attempts have been made to correlate the effects of substituents upon many types of side chain reactions under a single comprehensive theory. Williams[2] classifies reactions into three groups according to the effect on their rate by polar substituents: (A) those favored by accession of electrons to the point of reaction; (B) those favored by recession of electrons from the point of reaction; (C) those in which the data available are insufficient to classify in either group A or B.

Of the three esterification studies which Williams cites, he places two, those by Goldschmidt[3] and Kailan[4] in Group C. The third by Michael[5] is placed in group B, i. e., the esterification reaction was accelerated by a substituent such as the nitro group.

Hammett[6] has expressed the effect of a substituent in the meta or para position on the benzene ring upon the rate of a side chain reaction by the equation $\log k = \log k_0 + \sigma\rho$, where σ is a constant depending upon the substituent and ρ is a constant depending upon the reaction, medium, and temperature, k is the velocity constant for the substituted reactant and k_0 the constant for the unsubstituted reactant.

For a series of thirty-nine reactions (including equilibrium as well as velocity constants) the equation was found to predict the constants for the substituted reactants with a probable error for $\log k$ of less than 0.1 in thirty-three of the thirty-nine reactions. The only esterification work to which the equation was applied was that of Goldschmidt[3] and the probable error in $\log k$ was 0.118. The order of the effect of the different groups as found by Goldschmidt is quite different than that followed in the majority of the reactions cited by Hammett. The values of σ used by Hammett were determined from the data

(1) This paper is constructed from a dissertation presented by Alvin M. Borders to the Faculty of the Graduate School of Indiana University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Williams, *J. Chem. Soc.*, 37 (1930).

(3) Goldschmidt, *Ber.*, **28**, 3220 (1895).

(4) Kailan, *Ann.*, **351**, 186 (1907).

(5) Michael and Oeschlin, *Ber.*, **42**, 317 (1909).

(6) Hammett, THIS JOURNAL, **59**, 97 (1937).