[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Non-Aqueous Solutions. III. Some Organo-sodium Compounds in Ether

BY NORMAN B. KEEVIL AND HENRY E. BENT

Preliminary measurements[1] indicated that the value of 10^{-4} assumed for the dissociation constant of sodium triphenylmethyl in the calculation of the electron affinity of triphenylmethyl[1a] is far too high. The dissociation constants for this compound and certain related ones have, therefore, now been measured by a conductance method. The compounds selected were those for which the free energy of addition of sodium had been measured by two different methods,[1b] for the purpose of determining the electron affinity of the free radical. As this work has been discontinued it appears desirable to report the results which have been obtained.

Experimental

The cell was modeled after that previously described,[2] except that three platinum plates 3 × 4 cm. were used. The two outer ones were connected and all three were firmly held in place with a separation of about 1 mm. The cell constant was obtained by comparison with one of Professor Jones' conductivity cells, having a cell constant of 0.489804, using dilute potassium chloride solutions. When end effects were eliminated by having the upper surface of liquid more than 1 cm. above the plates, the measurements were reproducible to 0.01%. The cell constants for different cells were 0.003688, 0.003437 and 0.003847.

Adsorbed water was removed from the glass[3] by baking the entire cell and calibration bulb, after the system had been evacuated, in a large electrically heated furnace at about 450°. A siphoning arrangement somewhat similar to that of Kraus and Fuoss[4] was used for dilutions. The accuracy of the dilution is about 0.25% but at concentrations less than 10^{-7} g. equiv. per liter the combined errors of dilution and resistance measurements may amount to 10%.

Resistances up to 10^6 ohms were measured by using a vacuum tube oscillator and a Leeds and Northrup–Jones bridge combined with Shallcross resistors. The method of measuring higher resistances by the d. c. deflection method was modified so as to minimize polarization effects.[5] To measure resistances by this method, an e. m. f. was applied through the potentiometric circuit so that a deflection of about 40 cm. on the galvanometer scale was given. A Wolff potentiometer reading directly to 0.01 mv. was used to apply a variable potential to the cell. In series with the cell was a L. & N. type HS galvanometer, mounted on a Julius suspension. This instrument has a sensitivity of 1 mm., for 10^{-11} amp., and has a period of about forty seconds. The deflection given by the cell being roughly determined, the resistance of a large external slide resistor (5 and 125 megohm Cenco slide resistors) was adjusted to give the same deflection with the same potential. This resistor was adjusted until no deflection was obtained on rapidly switching over to the cell. The Cenco slide resistor was then compared with a suitable standardized Shallcross resistor by determining the voltage necessary to give the same deflection. The resistance of the cell was then calculated by Ohm's law. This calibration with a known resistor was made after every determination, being more reliable than a galvanometer sensitivity calibration curve. Polarization resistance did not cause drifting until the current had passed through the cell for four or five seconds. To minimize polarization effects, the lead wires were changed so as to reverse the direction of the current every few readings.

The a. c. bridge method, the d. c. bridge method and the d. c. deflection method described above were compared at resistances in the neighborhood of a million ohms and were found to agree to better than 1%. However, larger errors may occur if care is not taken to minimize polarization of the electrodes. The error due to polarization in using the Jones bridge with d. c. current may be avoided in the final balancing by applying a potential for only a short time by tapping the sensitive key and reversing the direction of current at about every other trial. This method gave resistance values to within 3% of the a. c. values for the voltage range 0.005 to 22.5 v., being more accurate at the lower voltages and when applying potentials for a very short time. Holding the key down for any length of time caused deviations of the order of 100% due to polarization errors. The d. c. deflection method was checked satisfactorily against the bridge method up to two and a half million ohms.

TABLE I

COMPARISON OF METHODS OF MEASURING HIGH RESISTANCES

Compound	A. C. bridge method, ohms $\times 10^{-6}$	D. C. bridge method, ohms $\times 10^{-6}$	D. C. deflection method, ohms $\times 10^{-6}$
Sodium phenylbiphenyl-	0.906	0.91	
α-naphthyl methyl in ether	.930		0.940
Disodium tetraphenyl-	2.15		2.15
ethylene in ether	2.35		2.38

Discussion of Results

Since the plot of log Λ against log *c* shows no deviation from a straight line, some other method for obtaining Λ_0 must be used. Fortunately it is possible to obtain this value with sufficient

---

(1) Dorfman, Thesis, Harvard University, 1933.

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

(1b) Keevil and Bent, *ibid.*, **58**, 1228 (1936); **58**, 1367 (1936); Keevil, *ibid.*, **59**, 2104 (1937).

(2) Bent and Dorfman, *ibid.*, **57**, 1924 (1935).

(3) Bent and Lesnick, *ibid.*, **57**, 1246 (1935).

(4) Kraus and Fuoss, *ibid.*, **55**, 3614 (1933), and private communication.

(5) Developed in this Laboratory by Bent and Swift.

accuracy for our purposes by a consideration of the values obtained by Kraus and co-workers on similar compounds. We should use Kraus and Kahler's[6] results on sodium triphenylmethide in liquid ammonia were it not for the fact that they had difficulty in handling dilute solutions on account of instability. We will therefore consider their data on similar compounds. Values of Λ_0 and of the transference number for potassium nitrate enable one to calculate values of Λ_0, for a

$$\Lambda_0(NO_3^-)/\Lambda_0(K^+) = 1.006 \text{ at } -33°\,[7]$$

number of ions. These are given in Table II grouped in four classes. Instead of giving Λ_0, the values in the table are for Walden's constant, that is, the conductance multiplied by the viscosity of the solvent, in this case ammonia. The most surprising ion is the anilide. Its presence in the first group suggests that it is a sufficiently strong acid to ionize in liquid ammonia and hence produces some ammonium ion which contributes to the conductivity. The values for triphenylgermanide and triphenylmethide are enclosed in parentheses on account of the uncertainty in the experimental data. The true values may be considerably larger. With the aid of this table we choose for the triphenylmethide ion a value of 0.20 ± 0.05. The assigned probable error includes not only the rough experimental value but also the value for triphenyl-stannide ion. Combining this with the value for sodium ion gives a value for sodium triphenylmethide of 0.52 ± 0.05. The error in this estimate is quite insignificant for our purposes as it introduces an error in log K of less than 0.1 and hence about 0.1 kcal. in the value for the free energy change. We next calculate values for Λ_0 by using values for the viscosity of ether of 0.00284 at 0° and 0.00223 at 25° taken from "I. C. T." This gives for Λ_0 at 0° 188 and at 25° 239.

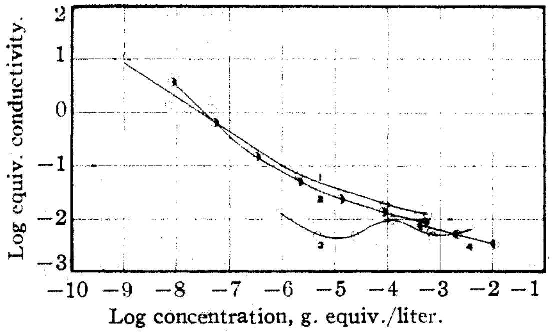


Fig. 1.—Conductances in ether solutions: 1, disodium tetraphenylethylene; 2, sodium phenylbiphenyl-α-naphthylmethide; 3, sodium phenylfluoride; 4, sodium diphenyl-α-naphthylmethide.

TABLE II

Values of the product obtained by multiplying the limiting conductance of the ion by the viscosity of the solvent (taken as 0.00256). Data are obtained from the work of Kraus and co-workers in liquid ammonia.[a]

Group 1 $\Lambda_0\eta > 0.4$, small ions		Group 2 $\Lambda_0\eta = 0.3$–0.4 includes cpds. with one phenyl	
K^+	0.420	Na^+	0.333
Rb^+	.453	$OC_{10}H_7^-$	.346
Cs^+	.431	$OC_{10}H_7^-$	.353
NO_3^-	.423	$SC_6H_5^-$	.371
$Sn(CH_3)_3^-$	.453	BrO_3^-	.379
$NHC_6H_5^-$	.476	$OC_6H_5^-$	.382
NH_2^-	.479	$SC_2H_5^-$	.387

Group 3 $\Lambda_0\eta = 0.25$–0.3, includes cpds. with two phenyls		Group 4 $\Lambda_0\eta < 0.25$ includes cpds. with three phenyls	
Li^+	0.287	$NH_2B(C_6H_5)_3^-$	0.217
$N(C_6H_5)_2^-$	.269		.238
	.261	$Sn(C_6H_5)_3^-$	.246
		$Ge(C_6H_5)_3^-$	.18 ± 0.02
		$C(C_6H_5)_3^-$	.15 ± 0.05

[a] Fuoss and Kraus, THIS JOURNAL, **55**, 1027 (1933); [b] Kraus and Hawes, *ibid.*, **55**, 2784 (1933); [c] Kraus and Kahler, *ibid.*, **55**, 3541 (1933); [d] Kraus and Johnson, *ibid.*, **55**, 3545 (1933).

The next step is to calculate values for the equilibrium constant at each concentration from the equation $K = (\Lambda/\Lambda_0)^2\, c$. Starting at high concentration the values of $-\log K$ are too small, due to the minimum in the conductance curve resulting from the presence of triple ions. As we proceed to more dilute solutions the values should approach a constant value. In the most dilute solutions where adsorbed material on the electrodes is being liberated and causing too high a conductance the values again become too small. Providing these two ranges do not overlap, the maximum value will then be the true value for the ionization constant. These results are given in Table III. Since we are dealing here with compounds which have at least three six-carbon rings in each ion we have used the same values for Λ_0 for all of the compounds.

The Effect of Temperature.—All of the compounds studied show decreasing ionization as the temperature is raised. We have not tried to estimate a value for Λ_0 for disodium tetraphenyl-

---

(6) Kraus and Kahler, THIS JOURNAL, **55**, 3537 (1933).

(7) Franklin and Cady, *ibid.*, **26**, 499 (1904).

TABLE III

CONDUCTANCE DATA AND VALUES FOR THE IONIZATION CONSTANT

Compound	Concn. in equiv. per liter $\times 10^6$		$\Lambda \times 10^2$		$-\log K$	
	25°	0°	25°	0°	25°	0°
Sodium phenyl-biphenyl-α-naphthylmethide	517	517	0.89	0.86	12.15	11.96
	82.3	78.7	1.38	1.36	12.56	12.39
	13.1	12.51	2.35	2.30	12.90	12.73
	2.08	1.99	5.00	4.60	13.04	12.93
	0.330	0.317	14.9	12.10	12.90	12.89
	.0525	.0506	81.7	71.3	12.42	12.13
	.0084	.0080	372	352	11.70	11.55
Sodium phenylfluoride	4,000	4,000	0.632	0.740	11.56	11.21
	3,200	601	.558	.653	11.76	12.15
	625		.468		12.48	
	601		.561		12.62	
	122		.978		12.69	
	23.8		.480		14.02	
	4.62		.427		14.84	
	0.904		1.32		14.56	
Sodium diphenyl-α-naphthylmethide	11,000	11,000	0.336	.379	11.66	11.35
	2,120	2,120	.512	.653	12.01	11.58
	410	410	.770	1.04	12.37	11.90
Sodium fluorenone	4,670	902	0.389	1.36	[a]	
	902		.908			
Disodium tetraphenylethylene	584	584	1.27	1.23		
	89.4	89.4	1.83	2.00		
	13.66	13.66	3.23	3.20		
	584	584	1.20	1.23		
	89.4	89.4	1.33	2.00		
	13.66	13.66	3.43	3.39		
	2.087	2.087	6.82	6.22		
	0.319	0.319	22.6	19.6		
	.0488	.0488	114	103		
	.00746	.00746	138	136		
	.00114	.00114	1,120	1,200		

[a] Values have not been calculated for the ionization constant for the last two compounds in the table on account of the uncertainty involved in the estimation of Δ.

ethylene at infinite dilution. However, the decrease in conductivity in going from 25 to 0° is not as great as would correspond to the increased viscosity of the ether and hence this compound must also ionize more at the lower temperature. This has been reported before for ether solutions[8] and is to be expected from the rapid change with temperature of the dielectric constant of ether. The value of $d\ln D/d\ln T$ is -1.29. Although the absolute values of $-\log K$ in the table are dependent on the value chosen for Λ_∞ the variation in $-\log K$ is much more precise and is accurate enough to give values for ΔH and ΔS for the process of ionization. These results are given in Table IV. These figures, although very meager, suggest that the free energy of dissociation will vary, depending on the distance of closest approach of the ions, as pointed out by Kraus and Fuoss, but that the entropy change, which is related to the orientation of the solvent, may be relatively constant.

An interesting effect of temperature was noted in the case of the ketyl obtained from fluorenone. After the resistance at 25° became constant, the cell was placed in a large Dewar at 0°. Instead of reaching an equilibrium value when temperature equilibrium was effected the resistance gradually decreased and did not begin to approach a constant value until about twenty-four hours had elapsed. Upon placing the cell again in the bath at 25° the original value for the resistance was obtained after about five hours. The cycle was repeated, the two rate curves checking within the accuracy of the determination of the zero of time in each case.

The curves obtained by plotting resistance against time may be rate curves for the reaction

---

(8) Bent and Dorfman, THIS JOURNAL, **57**, 1924 (1935); Coolidge and Bent, *ibid.*, **58**, 505 (1936).

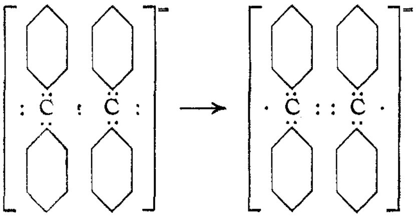
TABLE IV

VALUES OF ΔF, ΔH AND ΔS CALCULATED FROM THE IONIZATION CONSTANT

Compound	Temp., °C.	ΔF	ΔH	ΔS
Sodium phenyl-	25	21.9		
biphenyl-	12		−2.2	81
naphthyl-	0	19.9		
methide				
Sodium	25	24.4		
phenyl-	12		−0.7	83
fluoride	0	21.75		

of ionization, but the problem is complicated by the effect of the pinacolate which is undoubtedly present.

Tetraphenylethylene.—The remarkable behavior of disodium tetraphenylethylene deserves special mention. The slope of the curve on a plot of log Λ against log c is not $-1/2$ as would be expected from the mass law in dilute solutions but is $-2/3$. This behavior has been observed for disodium tri-α-naphthylboron but the explanation cannot be the same in the two cases. Tri-α-naphthylboron requires two electrons to complete its octet which it presumably gets from the two sodium atoms. The various quinonoid structures involving this pair of electrons result in a stabilizing resonance energy which explains the slope of $-2/3$ for this compound. In the case of disodium tetraphenylethylene, however, the loss of a single sodium ion releases a pair of electrons which would be expected to give rise to various quinonoid structures. In order for the second ionization constant to be as large or larger than the first some stabilization must be assumed to be possible within the molecule only when both sodium ions have been removed. The most obvious way of obtaining the necessary energy seems to be to assume the formation of the double bond in the ion which has lost both sodium ions, as in the structural formulas given below. Such a structure supplies far more than enough energy to account for the facts. Thus if we take the difference between a single and a double bond as about 67 kcal. and deduct 13 kcal. for the destruction of two electron pair, we have gained 54 kcal.[9] In addition we have the resonance energy due to the various structures in which the odd electron is at the ortho or para position of the benzene ring. Since it is likely that the resonance energy with a single electron will be very nearly the same as with an electron pair[10] the formation of the double bond would not alter the resonance energy. We therefore conclude that the negative ion of tetraphenylethylene contains a double bond. If this conclusion is correct, one would expect this compound to be highly colored in a solvent of high dielectric constant since the negative ion is a di-free radical. The fact is that this compound is highly colored even in ether solution, which confirms this hypothesis.



Summary

1. A method is described for measuring the conductance of a solution as a function of the concentration working in a closed system at very high dilutions.

2. Conductance data for the sodium salts of diphenyl-α-naphthylmethyl, fluorenone, phenylbiphenyl-α-naphthylmethyl, phenylfluoryl and tetraphenylethylene are reported.

3. The results are discussed with reference to the structure of the ions and the role of the solvent.

CAMBRIDGE, MASS.
UNIVERSITY OF MISSOURI
COLUMBIA, MO.
RECEIVED AUGUST 5, 1937

---

[9] This 13 kcal. is twice the difference between the electron affinity of triphenylmethyl and triphenylboron. [Bent and Dorfman, THIS JOURNAL, **57**, 1259 (1935).] Unpublished data indicate that the ionization constants for these two compounds are nearly the same so that we may take this difference as a rough measure of the relative stability of seven and eight electrons, respectively.

[10] Pauling and Wheland, *J. Chem. Phys.*, **3**, 315 (1935).