with benzene in alkaline solution,[15] and was reduced to 3-aminobiphenyl which was diazotized and added to boiling 30% sulfuric acid[16] to give 3-hydroxybiphenyl.

Four grams of potassium 2-chloro-4-phenylbenzoate, 3 g. of 3-hydroxybiphenyl and a methanol solution of sodium methylate prepared from 0.35 g. of sodium were placed in a flask, sufficient methanol being used so that the contents dissolved on refluxing. About 0.1 g. of copper powder was then added and the methanol removed by distillation, after which the flask was placed in an oil-bath and the temperature gradually raised. The reaction takes place readily at 150° and when the temperature of the bath reached 180° the flask was removed and the contents dissolved in about two liters of water containing a few grams of potassium hydroxide, after which the solution was filtered and the 2-(3′-phenylphenoxy)-4-phenylbenzoic acid precipitated with hydrochloric acid. Recrystallization from benzene or alcohol gave small, colorless needles which melted at 186–187°; yield 50–60%.

Anal. Calcd. for $C_{25}H_{18}O_3$: C, 81.93; H, 4.95. Found: C, 81.52; H, 4.95.

3,6-Diphenylxanthone.—Ring closure of 2-(3′-phenylphenoxy)-4-phenylbenzoic acid was accomplished with phosphorus pentachloride and aluminum chloride following the procedure described for the preparation of 3-phenylxanthone. A quantitative yield of crude material was obtained which appeared to be a mixture of 3,6-diphenylxanthone and 1,6-diphenylxanthone. Crystallization of this mixture from 1:1 methanol–benzene gave about a 35% yield of colorless needles which melted at 193.5–194.5°. The reasons for believing this compound to be 3,6-diphenylxanthone have been stated previously. The isomeric 1,6-diphenylxanthone was not obtained in pure form.

Anal. Calcd. for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 85.56; H, 4.64.

3,6,9-Triphenylxanthenol.—3,6-Diphenylxanthone, dissolved in benzene, was added to an ether solution of excess phenylmagnesium bromide and the mixture refluxed for about an hour. The product was decomposed with ammonium chloride and ice, and the ether extract concentrated and steam distilled. Crystallization of the residue from benzene gave colorless crystals which decomposed at 238–239°; yield 90%. With concentrated sulfuric acid, the carbinol gives a light red color with yellow-green fluorescence.

Anal. Calcd. for $C_{31}H_{22}O_2$: C, 87.29; H, 5.20. Found: C, 86.90; H, 5.32.

3,6,9-Triphenylxanthene.—3,6,9-Triphenylxanthenol was reduced to 3,6,9-triphenylxanthene by formic acid using the procedure previously described. Crystallization from benzene–petroleum ether gave small colorless plates which decomposed at 220°; yield 95%.

Anal. Calcd. for $C_{31}H_{22}O$: C, 90.69; H, 5.41. Found: C, 90.24; H, 5.42.

Summary

The reaction between 9-phenylxanthyl chloride and phenylmagnesium bromide has been studied, and it has been found that the chloride reacts largely in a quinonoid form and only to a limited extent in the benzenoid form. A number of xanthene derivatives have been prepared and described.

ANN ARBOR, MICH. RECEIVED DECEMBER 21, 1936

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[15] Blakey and Scarborough, *J. Chem. Soc.*, 3000 (1927).

[16] Jacobsen and Loeb, *Ber.*, **36**, 4083 (1903).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Structure of Metal Ketyls. V. The Conductance Function

BY CHARLES BUSHNELL WOOSTER

I. Introduction

Previous papers in this series[1] have reported some studies of the chemical reactions of monosodium benzophenone in liquid ammonia solution. It has become increasingly evident that such solutions comprise a system of rather complex equilibria and that further progress on the problem of the structure of metal ketyls would be facilitated greatly by more accurate information regarding the nature and interrelations of these equilibria. It is the purpose of the present paper to show that the conductance of sodium benzophenone in liquid ammonia as measured by Kraus and Bien[2] may be described quantitatively by assuming the presence of the following equilibria

$$[(C_6H_5)_2CO]Na \rightleftharpoons [(C_6H_5)_2CO]^- + Na^+ \quad (1)$$

$$2[(C_6H_5)_2CO]Na \rightleftharpoons (C_6H_5)_2C(ONa){-}C(ONa)(C_6H_5)_2 \quad (2)$$

$$(C_6H_5)_2C(ONa){-}C(ONa)(C_6H_5)_2 \rightleftharpoons Na^+ + Na[(C_6H_5)_2CO]_2^- \quad (3a)$$

$$[(C_6H_5)_2CO]Na + [(C_6H_5)_2CO]^- \rightleftharpoons Na[(C_6H_5)_2CO]_2^- \quad (3b)$$

that is, simple ionization of the metal ketyl (1), association of the metal ketyl molecules (ion pairs) to the un-ionized pinacolate (2), and formation of

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[1] (a) Wooster, THIS JOURNAL, **51**, 1858 (1929); (b) Wooster, *ibid.*, **56**, 2436 (1934); (c) Wooster and Holland, *ibid.*, **56**, 2438 (1934); (d) Wooster and Dean, *ibid.*, **57**, 112 (1935).

[2] (a) Kraus and Bien, *ibid.*, **55**, 3609 (1933); (b) Bien, Dissertation, Brown University, 1932.

triple ions by primary ionization of the pinacolate (3a) or by reaction between simple metal ketyl anions and metal ketyl ion pairs (3b). Only three of these four equilibria are independent and for the purpose of mathematical convenience equilibrium 3b has been chosen in preference to 3a as the basis of analysis; the reasons for omitting equilibria involving doubly charged pinacolate anions are discussed in the fourth section of this paper.

Kraus and Bien found that the conductance curve did not correspond to a simple binary equilibrium (as, for instance, that expressed in equation 1), and also noted that the equivalent conductance was much higher than that of the structurally similar salt, sodium benzohydrolate, at corresponding concentrations. They did not attempt further analysis of the conductance curve. According to the present interpretation the higher conductance may be attributed[3] in part to the presence of the third ionic species (triple ions) formed in accordance with equation 3b. This triple ion equilibrium bears a formal resemblance to that discussed by Fuoss and Kraus[4] but is distinctly different in two important respects. First, the triple ion formation is in the present instance due primarily to the quantum forces involved in the formation of a carbon–carbon bond. It is this fact which permits these triple ions to play an important part in the conduction process at concentrations between 0.01 and 0.0001 N in liquid ammonia where the formation of triple ions as the result of coulomb forces alone is excluded by the high dielectric constant of the medium. Second, these quantum forces operate only between the ion pair and an *anion;* there is no corresponding tendency toward triple ion formation by combination of an ion pair with a cation. As a result of this unilateral triple ion formation, the conductance function differs from that deduced by Fuoss and Kraus[4] for bilateral triple ion formation.

In Section II the conductance function for unilateral triple ion formation is derived and compared with the experimental results in the region 0.001–0.0001 N where the influence of the equilibrium expressed in equation 2 is negligible. In Section III the association of the ion pairs is considered and in Section IV the bearing of the results on the problem of the structure of the metal ketyls is discussed.

II. Unilateral Triple Ion Formation

For simplicity and for convenient comparison with the equations of Fuoss and Kraus we shall first consider the case of very low ion concentrations, where the activity coefficients and (square root) mobility corrections may be set equal to unity, and where the fraction of solute present as ions may be neglected in comparison with unity.

Abbreviating the simple ions as A^+ and B^- and representing the complex species in a corresponding manner, the mass action equation for the binary equilibrium

$$[A^+][B^-]/[AB] = K \qquad (4)$$

then reduces to

$$C\gamma(\gamma + \gamma_3) = K \qquad (5)$$

where C is the total concentration, K is the mass action constant, and γ and γ_3 are the ratios of the concentrations of the simple anions and the triple anions, respectively, to the stoichiometric concentration.[5]

The mass action equation for the triple ion formation

$$[AB][B^-]/[AB_2^-] = k \qquad (6)$$

reduces to

$$C\gamma/\gamma_3 = k,\ \gamma_3 = C\gamma/k \qquad (7)$$

and the observed conductance Λ is given by

$$\Lambda = \gamma\Lambda_0 + \gamma_3\lambda_0 \qquad (8)$$

where Λ_0 is the sum of the limiting conductances of the two simple ions, and λ_0 the sum of the limiting conductances of the triple ions and of the simple cations.

Solving equations 5 and 7 for γ and γ_3, substituting in equation 8 and simplifying gives

$$\Lambda(1 + C/k)^{1/2} = (\Lambda_0\sqrt{K})/\sqrt{C} + (\lambda_0\sqrt{K}/k)\sqrt{C} \qquad (9)$$

which differs from the corresponding equation of Fuoss and Kraus[6] by the coefficient of Λ. This coefficient prevents the equation from assuming a linear form on multiplication by $\sqrt{C}$, but a linear equation may be obtained from equation 9 in the following way. If we multiply equation 9 by $\sqrt{C}$, add and subtract $(C\Lambda_0\sqrt{K}/k)$ on the right-hand side of the equation, divide by $(1 + C/k)^{1/2}$, square both sides and simplify, we obtain

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(3) This interpretation supersedes the suggestion made in the previous paper, ref. 1d. However, it is possible that a part of this higher conductance may be due to a resonance phenomenon (discussed in the latter part of this paper) and therefore to this extent it may be the result of a certain analogy between sodium benzophenone and sodium triphenylmethyl.

(4) Fuoss and Kraus, THIS JOURNAL, 55, 2387 (1933).

(5) If C represents the total concentration in equivalents (as AB) per liter and the quantities in brackets represent concentrations of the included species, then $[B^-] = C\gamma$, $[AB_2^-] = C\gamma_3$, $[A^+] = C(\gamma + \gamma_3)$ and $[AB] = C(1 - \gamma - 2\gamma_3)$. In the simplified expressions above $(1 - \gamma - 2\gamma_3)$ is set equal to unity.

(6) Ref. 4, equation 4.

$$C\Lambda^2 = \Lambda_0^2K + [2\lambda_0/\Lambda_0 - 1 + (1 - \lambda_0/\Lambda_0)^2/(1 + k/C)]\Lambda_0^2KC/k \quad (10)$$

The term $(1 - \lambda_0/\Lambda_0)^2/(1 + k/C)$ becomes negligible at sufficiently low concentrations and at high concentrations approaches asymptotically the limit $(1 - \lambda_0/\Lambda_0)^2$. Accordingly, this entire term may be neglected when the value of λ_0/Λ_0 is sufficiently close to unity to render $(1 - \lambda_0/\Lambda_0)^2$ negligible with respect to $(2\lambda_0/\Lambda_0 - 1)$. Under these conditions equation 10 assumes the following form which is linear with respect to the variables $C\Lambda^2$ and C.

$$C\Lambda^2 = \Lambda_0^2K + C(2\Lambda_0\lambda_0 - \Lambda_0^2)K/k \quad (11)$$

This equation is, of course, applicable only to instances of unilateral triple ion formation at low total ion concentrations as for instance in dilute solution in a solvent of low dielectric constant. In order to apply it to solutions in solvents of higher dielectric constant such as liquid ammonia it is necessary to include the interionic terms in $\sqrt{C}$ in activity and mobility as well as the fraction of un-ionized solute which may no longer be set equal to unity. These corrections may be approximated in the manner of Fuoss and Kraus[4] by substituting $2C\Lambda/\Lambda_0$ for the ion concentration $2C(\gamma + \gamma_3)$ in the usual formulas and applying the results as appropriate correction terms to (11).

If the various corrections are made to (5), (7) and (8), by introducing the activity coefficient f defined by the relation $-\log f = \beta\Lambda_0^{-1/2}\sqrt{C\Lambda}$, a mobility coefficient $m = 1 - \alpha\Lambda_0^{-3/2}\sqrt{C\Lambda}$ and the term $(1 - \Lambda/\Lambda_0)$ as an approximation for the un-ionized fraction of the solute, we obtain

$$\begin{aligned} &Cf^2\gamma(\gamma + \gamma_3)/(1 - \Lambda/\Lambda_0) = K \\ &C\gamma(1 - \Lambda/\Lambda_0)/\gamma_3 = k \\ &\gamma_3 = C\gamma(1 - \Lambda/\Lambda_0)/k, \text{ and} \\ &\Lambda = m(\gamma\Lambda_0 + \gamma_3\lambda_0) \end{aligned}$$

Combining these equations[7] yields the corrected form of equation 11

$$\left(\frac{f\Lambda}{m}\right)^2 \frac{C}{(1 - \Lambda/\Lambda_0)} = \Lambda_0^2K + \frac{(2\Lambda_0\lambda_0 - \Lambda_0^2)K}{k}\left(1 - \frac{\Lambda}{\Lambda_0}\right)C \quad (12)$$

Comparison with Experiment.—In order to apply equation 12 to the conductance data on monosodium benzophenone, it is necessary to choose a value for Λ_0. As a matter of fact, the linearity of the equation is not very sensitive to the value of Λ_0 chosen, which therefore need only be approximate. In consequence, however, equation 12 is of little assistance in suggesting a choice of Λ_0. Fortunately this constant may be closely approximated from a knowledge of the conductance of similar salts in liquid ammonia. The limiting equivalent conductance of the sodium ion in liquid ammonia[8] is known to be 130 and the limiting equivalent conductances, Λ_0', of a number of anions in liquid ammonia[8] are collected in Table I.

TABLE I

CONSTANTS OF ELECTROLYTES IN AMMONIA

No.	Salt	Λ_0	Λ_0'	$K \times 10^4$	$a \times 10^8$
1	KNH_2	351	187	0.7	2.2
2	$NaNHC_6H_5$	316	(186)	8.2	3.1
3	$NaOC_6H_5$	279.4	149.3	3.82	2.7
4	$NaN(C_6H_5)_2$	235	105	58	6.7
5	$KN(C_6H_5)_2$	266	102	50.5	6.0
6	$NaSn(C_6H_5)_3$	226	96	130	(10.4)
7	$KNH_2\cdot B(C_6H_5)_3$	257	93	130	10.4
8	$NaNH_2\cdot B(C_6H_5)_3$	215	85	150	10.9

Since the values of Λ_0' in a given solvent at a fixed temperature are doubtless primarily determined by the size of the migrating ion, the value of Λ_0' for the ion $[(C_6H_5)_2CO]^-$ may be expected to lie between the limits 96 and 105 and to be closer to the upper than to the lower limit. For purposes of calculation the upper value has been chosen so that $\Lambda_0 = 235$. The value of λ_0' may be estimated from the assumed value of Λ_0 by means of Stokes's law to be approximately 77, corresponding to $\lambda_0 = 207$. On this basis, the maximum alteration in the slope of the plot due to the neglected term of equation 10 would be 1.87%, which is well within the limits of experimental error.

A plot of $f^2C\Lambda^2/m^2(1 - \Lambda/\Lambda_0)$ against $C(1 - \Lambda/\Lambda_0)$ appears in Fig. 1 and, in conformity with the requirements of equation 12, this plot is linear throughout the dilution range 10^3–10^4 liters. The values of the constants obtained from the intercept and slope are, respectively, $\Lambda_0^2K = 5.6$ and $(2\Lambda_0\lambda_0 - \Lambda_0^2)K/k = 2.4 \times 10^3$. Introducing the estimated values of Λ_0 and λ_0, the following values are obtained for the mass action constants: $K = 1.01 \times 10^{-4}$ and $k = 1.8 \times 10^{-3}$.

III. The Association of Ion Pairs

At concentrations above 0.001 N the equivalent conductance of monosodium benzophenone falls below that predicted by equation 12. This deviation may be due in part to the failure at higher ion concentrations of the approximations intro-

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(7) The coefficients α and β have the same significance as in the paper of Fuoss and Kraus [THIS JOURNAL, **55**, 476 (1933)]. In liquid ammonia at its boiling point $\alpha = 2.133\Lambda_0 + 442$ and $\beta = 4.742$.

(8) Fuoss and Kraus, *ibid.*, **55**, 1027 (1933); Kraus and Hawes, *ibid.*, **55**, 2784 (1933); Kraus and Kahler, *ibid.*, **55**, 3541 (1933); Kraus and Johnson, *ibid.*, **55**, 3545 (1933).

duced in the estimate of the activity and mobility terms, etc. However, these deviations seem to be much larger than would be expected on this basis alone and it is likely that they are due primarily to a reduction in the concentration of the ion pairs as the result of association in accordance with equation 2.

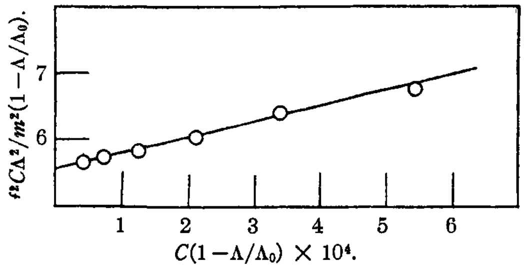

Fig. 1.—Unilateral triple ion formation.

Equation 12 may be corrected for this effect by introducing the term $C\gamma_2(1 - \Lambda/\Lambda_0)$ in place of $C(1 - \Lambda/\Lambda_0)$ for the concentration of the ion pairs, (γ_2 represents the fraction of non-conducting solute present as ion pairs) and assumes the form

$$\left(\frac{f\Lambda}{m}\right)^2 \frac{C}{(1-\Lambda/\Lambda_0)\gamma_2} = \Lambda_0{}^2K + \frac{(2\Lambda_0\lambda_0 - \Lambda_0{}^2)K}{k}\left(1 - \frac{\Lambda}{\Lambda_0}\right) C\gamma_2 \quad (13)$$

The mass action equation for ion pair association

$$[AB]^2/[A_2B_2] = k_4 \quad (14)$$

reduces to

$$2C\gamma_2{}^2(1-\Lambda/\Lambda_0)/(1-\gamma_2) = k_4 \quad (15)$$

and the required values of γ_2 could be obtained if k_4 were known. Conversely k_4 should be determined by the values of γ_2 required to satisfy equation 13. These may be obtained from the experimental results by substituting the constants as determined at lower concentrations in equation 13 and solving for γ_2. Since equation 15 may be transformed as follows

$$2C\gamma_2(1 - \Lambda/_0) = k_4/\gamma_2 - k_4 \quad (16)$$

the values of γ_2 may be tested for conformity with the mass action equation by plotting $2C\gamma_2(1 - \Lambda/\Lambda_0)$ against $1/\gamma_2$. The plot should yield a straight line crossing the $1/\gamma_2$ axis at unity and k_4 may be obtained from either the slope or the other intercept. Such a plot appears in Fig. 2 from which it is evident that the values of γ_2 comply satisfactorily with the stated requirements over the dilution range 50–800 liters, yielding the value $k_4 = 1.56 \times 10^{-2}$.

Calculation of the Conductance Curve.—The conductance curve may be calculated from the final conductance equation (13) in the following way. Abbreviating $C(1 - \Lambda/\Lambda_0)$ to x and substituting the values of the constants, equation 13 may be solved readily for $fC\Lambda/m$

$$fC\Lambda/m = \sqrt{5.6x\gamma_2 + 2400(x\gamma_2)^2} \quad (17)$$

and, similarly, equation 15 may be solved for γ_2

$$10^2\gamma_2 = -0.39/x + \sqrt{(0.39/x)^2 + 78/x} \quad (18)$$

Thus by substituting arbitrary values of x, the corresponding values of $fC\Lambda/m$ may be obtained from equations 18 and 17. Since $fC\Lambda/m$ is a function of $C\Lambda$ and known constants (Λ_0, β and α), the corresponding values of $C\Lambda$ may be read from a plot of $fC\Lambda/m$ against $C\Lambda$. The concentration corresponding to the chosen value of x is then given by $C = x + C\Lambda/\Lambda_0$ and Λ may be obtained from C and $C\Lambda$. Of course, for sufficiently low values of x it is possible to set $\gamma_2 = 1$ and dispense with the use of equation 18.

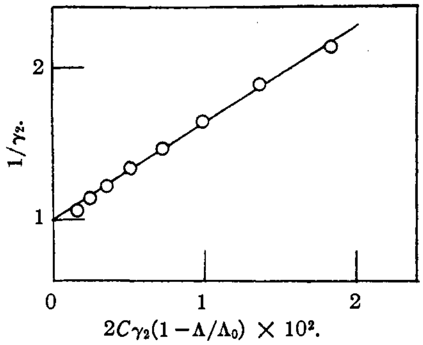

Fig. 2.—Ion pair association.

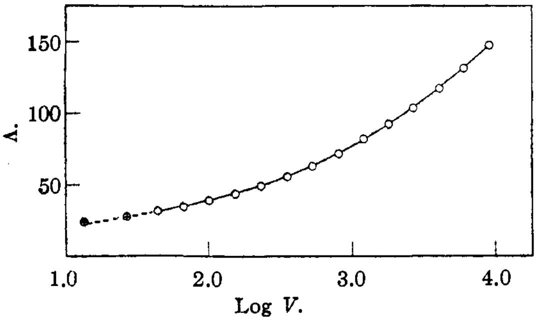

Fig. 3.—The conductance curve.

In Fig. 3 a plot of Λ against log V is shown in which the calculated values are represented by the continuous curve and the experimental values by the circles. In addition to the published values, Kraus and Bien obtained two series of lesser accuracy. These measurements show erratic deviations at high dilutions, but at higher concentrations, where they are more reliable, the two series agree with the calculated curve within the limits of experimental error. Two measurements from one of these series, which were made at higher concentrations than any of the published values, are indicated in Fig. 3 by the crossed circles and lie reasonably close to the calculated curve. The extrapolated portion of this curve is represented in the figure by a broken line.

IV. Discussion of Results

There can be no doubt that the final conductance equation adequately reproduces the experimental data and there is no reason to question the existence of the postulated equilibria involving the five solute species: AB, A_2B_2, A^+, AB_2^-, B^-. The existence of the simple ions and the corresponding ion pairs is indicated by all the well-known evidence in favor of the free radical nature of the metal ketyls, and association to the pinacolate (A_2B_2 or its ions) has been demonstrated both in ether[9] and in liquid ammonia solution.[1b] The omission of the sixth solute species (B_2^{--}, the doubly charged pinacolate anion) in the formulation of the conductance equation was based on the assumption that this ion would be too highly dissociated (in virtue of the electrostatic repulsion of the two negative charges) to play a significant part in the conduction process. Although there is no entirely independent evidence in support of this assumption, it is interesting to note that the assumption may be shown to be consistent with the observed values of the mass action constants.

The primary ionization constant of the pinacolate, K_4, may be calculated from the other three constants

$$[A^+][AB_2^{--}]/[A_2B_2] = K_4 = Kk_4/k = 8.75 \times 10^{-4}$$

and from this value the corresponding secondary ionization constant, $K_3 = [A^+]\ [B_2^{--}]/[AB_2^-]$, may be estimated roughly to be 5.23×10^{-7} by suitable modifications of the method of Fuoss and Kraus.[10] Since the concentration of sodium ions cannot be less than that of the triple anions ($[A^+] > [AB_2^-]$), the concentration of pinacolate anions, $[B^{--}]$, cannot exceed 5.23×10^{-7}. The ratio of the concentration of the pinacolate anions to that of the simple anions is proportional to the square root of the former

$$[B_2^{--}]/[B^-] = (K_3[B_2^{--}]/kK)^{1/2} = 1.7[B_2^{--}]^{1/2}$$

and on substituting 5.23×10^{-7} as the maximum value of $[B_2^{--}]$, the maximum value of the ratio is found to be 1.23×10^{-3}, which implies that only a negligible fraction of the current is carried by the doubly charged pinacolate anions at any concentration.

For these reasons we may proceed to discuss the significance of the results with respect to the structural problems of the metal ketyls on the assumption that the observed mass action constants represent the true values within the limits of error imposed by the approximations introduced in the correction terms for mobility, activity and un-ionized fraction.

The Structure of the Ion Pair.—Previous studies of the reaction between the metal ketyl and alkyl halides[1] have furnished evidence that the observed carbon alkylation occurs in the first step of the reaction, presumably as the result of a simple substitution process. On this basis, the suggestion was made that the charge on the metal ketyl anion was not located exclusively on the oxygen atom, but was "shared" to some extent with the extra-nuclear carbon. The available chemical evidence does not permit a precise definition of the term "shared"; this evidence is equally compatible with a model involving a triple electron bond between carbon and oxygen and with a resonance model,[11] including in the complete wave equation the structures $(C_6H_5)_2\underset{\cdot}{C}:\underset{\cdot\cdot}{\ddot{O}}:$ and $(C_6H_5)_2\underset{\cdot\cdot}{C}:\underset{\cdot}{\ddot{O}}:$ together with many others which locate the charge on quinonoid rings. Furthermore, the extent to which a similar sharing is involved in the structure of the ion pair is not revealed by the chemical evidence, for it is even conceivable that the ion pairs undergo alkylation only after a preliminary separation into free ions.[12]

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[9] Bachmann, THIS JOURNAL, **55**, 1179 (1933).

[10] Fuoss and Kraus, *ibid.*, **55**, 1021–1024 (1933). When one ion is doubly charged, equation 6 of Fuoss and Kraus assumes the form

$$K_3^{-1} = \frac{4\pi N}{1000}\left(\frac{2e^2}{DkT}\right)^3 Q(b)$$

where $Q(b)$ is the function tabulated by these authors and $b = 2e^2/aDkT$. In making the above estimate, the fact that the two charges in the pinacolate anion are not located at the same point was ignored. This corresponds very crudely to the assumption that the sodium ion is equidistant from the two negative charges in the triple ion. The value used for the parameter a was that corresponding to the primary ionization constant, K_4. Since K_4 is greater than K, it is possible that repulsion between the sodium ions in the pinacolate may play a part in determining K_4. Such repulsion is absent in the triple ion and *on this basis* it would be predicted that the parameter a corresponding to K_3 should be less than that assumed and, accordingly, the estimated value of K_3 might be regarded as a maximum.

[11] (a) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933); (b) Bent and Keevil, *ibid.*, **58**, 1370 (1936).

[12] It is, perhaps, desirable to state here that the phrase "carbon–sodium bond in the metal ketyl" used in the previous paper of this series (ref. 1d) was not intended to refer specifically to the ion pair. In fact, it was immediately elaborated in terms of the free anion. It was used as a general term to designate a structural fea-

Fuoss and Kraus[10] have derived an expression relating the dissociation constant of an ion pair to a parameter a which may be considered as the minimum distance of separation of the positive and negative charges in an ion pair formed from spherical ions. Although the significance of a cannot be so simple when unsymmetrical ions are involved, it seems reasonable to suppose that even in such cases a is primarily determined by this minimum distance.[13] Accordingly it is interesting to compare the a value for the metal ketyl ion pair with the estimates of those corresponding to the ionization of sodium benzohydrolate, $(C_6H_5)_2CHONa$, and the primary ionization of disodium benzophenone, $(C_6H_5)_2CNaONa$, which appear in Table II.[14]

TABLE II

CONSTANTS OF SODIUM BENZOPHENONE AND RELATED SALTS IN LIQUID AMMONIA

No.	Salt	$K \times 10^4$	$a \times 10^8$
1	$[(C_6H_5)_2CHO]Na$	0.32	2.01
2	$[(C_6H_5)_2CO]Na$	1.01	2.28
3	$[(C_6H_5)_2CONa]Na$	3.2	2.70

In the sodium benzohydrolate ion pair the sodium ion is presumably located in the vicinity of the oxygen atom which carries the anionic charge. The a value for this salt, lower than any listed in Table I, is entirely compatible with this model, for it indicates the absence of the steric factors which, coming into play on closer approach of the sodium ion to the phenyl groups, result in the much larger a value of sodium diphenylamide. The very low a value is probably also due in part to specific influences resulting from the location of the charge on oxygen, as is suggested by comparison of the a values for the similarly constituted sodium phenolate and sodium anilide (nos. 3 and 2, Table I).

The primary ionization of disodium benzophenone is in some respects the closest available analog of the ionization of a metal ketyl ion pair in which the charge is effectively located on the extra-nuclear carbon, but it is probable that the a value is somewhat lower than that which would correspond to the ionization of such a metal ketyl ion pair.[15] Nevertheless, the fact that the observed a value for the actual metal ketyl ion pair lies between the other two listed in Table II is qualitatively significant and may be interpreted in two ways. First, the actual structure of the metal ketyl ion pair may not correspond to a model in which the sodium ion is definitely located in the vicinity of the oxygen (*i. e.*, analogous to sodium benzohydrolate) or to one in which the sodium ion is located in the vicinity of the extra-nuclear carbon, but it may, instead, possess an intermediate character. If the a values are assigned quantitative significance, the intermediate structure would appear to be approximated more closely by the first model. Second, the structure of the metal ketyl anion may correspond to the resonance model, previously mentioned, and the sodium ion may be definitely located in the vicinity of the oxygen in the ion pair. On this basis, the increase in the a value over that of sodium benzohydrolate can be ascribed to the coulomb interaction of the sodium ion and the electrons which may be considered to give rise to resonance in the

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ture which might characterize either the ion pair, the free anion or both. From this point of view, it is evident that the conclusions of Bent (ref. 11b) regarding the structure of the ion pair are restrictive rather than contradictory. Further discussion regarding the relation between the chemical evidence and the structure of the ketyl anion will be reserved for a subsequent paper.

(13) As calculated from dissociation constants by Coulomb's law, the parameter a gives the diameter of a fictitious sphere which will duplicate the properties of the real physical system. Since a strictly accurate calculation should involve a form factor, the omission of this factor in the present theory is absorbed in the numerical value of a. Consequently, any space factor (steric hindrance) which would decrease the probability of formation of ion pairs will appear as a numerically larger a value than that corresponding to the actual atoms on which the charges are located.

(14) The data on the conductance of sodium benzohydrolate in liquid ammonia[2] are not sufficiently accurate to permit the precise determination of Λ_0 by extrapolation. By the use of the approximate formula

$$K = \left(\frac{f\Lambda}{m\Lambda_0}\right)^2 \frac{C}{(1 - \Lambda/m\Lambda_0)}$$

setting $\Lambda_0 = 235$, the value of $K \times 10^4$ for this salt was found to lie between 0.29 and 0.35 over the dilution range 616–6450 liters per mole. The average of ten determinations from two independent series of measurements was 0.32. The data on disodium benzophenone were treated in a similar way, attributing all of the conductance to the primary ionization (in order to obtain a maximum value of K for this process) and setting $\Lambda_0 = 221$ (estimated for $[Na^+][(C_6H_5)_2CONa]^-$ by means of Stokes' law). The resulting values of $K \times 10^4$ fell between the limits 2.8 and 3.7 over the dilution range 96–1700 liters per mole and the average of nine determinations from two independent series was 3.2.

(15) Two disturbing factors which are absent in such a metal ketyl ion pair may play a significant part in the determination of the a value found for disodium benzophenone. The fact that this primary dissociation may lead to the formation of two types of anions might be expected to result in greater ionization and accordingly to a somewhat larger a value than would otherwise be the case. On the other hand, it seems likely that in any reasonable models of un-ionized disodium benzophenone which locate one sodium ion in the vicinity of the extra-nuclear carbon and the other in the vicinity of the oxygen, the first sodium ion will be closer to the negatively charged oxygen than to the other sodium ion. Accordingly, the resultant influence of the sodium–oxygen dipole on the first sodium ion will be an attraction and will tend to reduce the ionization and the corresponding a value. Since this effect is fundamentally similar to that responsible for bilateral triple ion formation which does not occur extensively except in solvents of much lower dielectric constant, it would be expected to reduce the a value by only a moderate amount, yet it appears to counteract both the first disturbing influence mentioned above as well as at least a part of the steric hindrance of the phenyl groups.

metal ketyl anion as a result of their wandering around in the benzene rings.[11b] This coulomb interaction would tend to localize the charge electron in the vicinity of the sodium ion so that the ion pair would be formed at the expense of some of the resonance energy of the anion, and the resulting instability of the ion pair would be revealed by an increase in the values of K and a. The difference between the a values of the metal ketyl and of sodium benzohydrolate corresponds to an energy difference of 0.55 kcal., which could be considered as an approximate measure of the *minimum*[16] contribution of the charge electron to the resonance energy of the free anion. The conductance data furnish no basis for a decision between these two interpretations, but the evidence advanced by Bent[11b] establishes a presumption in favor of the second hypothesis. It should be noted, however, that these alternative hypotheses are merely limiting cases since the two factors suggested as possible causes of the increased a value are not, necessarily, mutually exclusive.

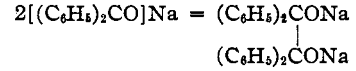
The Association of Ion Pairs.—The mass action constants k and k_4 are much more sensitive than K to errors[17] in the approximations introduced in applying the conductance equation and are, perhaps, reliable only as to order of magnitude. The independent evidence regarding association to the pinacolate in 0.3 normal solution, presented in the second paper of this series,[1b] indicated a much lower degree of association than is obtained by extrapolation to that concentration using these observed values of the mass action constants. Although such extrapolation is justified only as a crude approximation, it is unlikely that the discrepancy is due entirely to the uncertainties in the constants or in the extrapolation. It is probable that the actual proportion of pinacolate in such concentrated solutions is higher than was indicated by the application of a modification of Bachmann's method[9] to liquid ammonia solutions, and that a considerable fraction of the pinacolate dissociated during the decomposition with ammonium chloride.

Summary

1. It has been shown that the conductance of sodium benzophenone in liquid ammonia may be described quantitatively by assuming the presence of the following equilibria

$$[(C_6H_5)_2CO]Na = [(C_6H_5)_2CO]^- + Na^+$$

$$[(C_6H_5)_2CO]Na + [(C_6H_5)_2CO]^- = Na[(C_6H_5)_2CO]_2^-$$



$$2[(C_6H_5)_2CO]Na = \begin{array}{l}(C_6H_5)_2CONa \\ \quad\ \ | \\ (C_6H_5)_2CONa\end{array}$$

2. The structure of the ion pair has been discussed. The available evidence is consistent with the hypothesis that the sodium ion is located in the vicinity of the oxygen in the ion pair, provided it is further assumed that this ion pair is formed at the expense of some of the resonance energy of the free anion and that the charge electron participates in the resonance phenomenon in this anion.

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[16] The coulomb interaction may cancel only a fraction of the contribution of the charge electron to the resonance energy.

[17] It seems likely that such errors can be reduced by using a solvent of lower dielectric constant. Accordingly, an attempt will be made to measure the conductance of metal ketyls in pyridine.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Dissociation Constants of Diaquotetrammine Cobaltic Cation as an Acid

BY ARTHUR B. LAMB AND EDWIN B. DAMON

Diaquotetrammine cobaltic ion may be regarded, in accordance with Brønsted's definition, as a cation acid which dissociates in two steps as follows

$$[Co(NH_3)_4(H_2O)_2]^{+++} \longrightarrow [Co(NH_3)_4(H_2O)(OH)]^{++} + H^+$$

and

$$[Co(NH_3)_4(H_2O)(OH)]^{++} \longrightarrow [Co(NH_3)_4(OH)_2]^{+} + H^+$$

Brønsted and his collaborators[1] have measured the primary dissociation constants of this and of a number of similar aquo ion acids and have found interesting differences among them. Their measurements, in the case of the diaquotetrammine cation, were carried out by two independent methods. In the first method, the solubility of the slightly soluble diaquotetrammine salt of the oxalodinitrodiammine cobaltic anion was measured in solutions of varying known acidity; this was compared with the solubility of the luteo salt under similar conditions. In the

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[1] J. N. Brønsted and C. V. King, *Z. physik. Chem.*, **130**, 699 (1927); J. N. Brønsted and K. Volqvartz, *ibid.*, **134**, 97 (1928).