CHEMICAL EDUCATION

(67) A Problem in Laboratory Administration—Its Solution, *Science*, **30**, 699 (1909).

(68) Laboratory Exercises in General Chemistry—Transition Point, Suspended Transformation, Law of Successive Reactions, *School Science and Mathematics*, **14**, 402 (1914).

(69) A Student Apparatus to Illustrate Diffusion of Gases, with Chas. R. Parkinson, *School Science and Mathematics*, **14**, 40 (1914).

(70) Laboratory Exercise in Atomic Structure, with J. E. Day, *J. Chem. Educ.*, **1**, 100 (1924).

(71) The Vapor Density of Steam, with J. E. Day, C. S. Pease and G. D. Bland, *J. Chem. Educ.*, **1**, 152 (1924).

(72) The Determination of the Formula of Carbon Dioxide with J. B. Peterson, H. B. Hass, G. P. Hoff and J. E. Day, *J. Chem. Educ.*, **2**, 932 (1925).

(73) Vapor Density of Steam, with C. S. Martin and J. E. Day, *J. Chem. Educ.*, **6**, 107 (1929).

(74) Experiment in Cooperative Teaching, with J. E. Day, *J. Chem. Educ.*, **5**, 1133 (1928).

(75) The Preparation of Wood Char, with J. E. Day, *J. Chem. Educ.*, **5**, 350 (1928).

(76) Memorials in Chemical Laboratories, with J. E. Day, *J. Chem. Educ.*, **6**, 332 (1929).

(77) Experiences Teaching Proficiency Students in Chemistry, with W. C. Fernelius and L. L. Quill, *J. Chem. Educ.*, **14**, 427–433 (1937).

BOOKS

(78) "Study and Quiz Outline," Ginn and Co., Boston, Mass., 1923.

(79) "Laboratory Manual," with Wm. McPherson and W. E. Henderson. Ginn and Co., Boston, Mass., 1929.

(80) "An Elementary Course in Qualitative Analysis," with J. E. Day and A. B. Garrett. Ginn and Co., Boston, Mass., 1938.

(81) "Semimicro Qualitative Analysis," with A. B. Garrett and L. L. Quill. Ginn and Co., Boston, Mass., 1940.

(82) "Semimicro Qualitative Analysis," with A. B. Garrett and H. H. Sisler. Ginn and Co., Boston, Mass., 1951.

BOOK REVIEWS

(83) "Chemistry in High Schools," by E. P. Schoch. University of Texas, Bulletin 210, Official Series, No. 64, VIII, 119. THIS JOURNAL, **35**, 98 (1913).

(84) "Notes on Elementary Inorganic Chemistry," by F. H. Jeffery. Cambridge University Press, G. P. Putnam's Sons, New York. THIS JOURNAL, **37**, 235 (1915).

(85) "Inorganic Chemistry," International Chemical Series by Hamilton P. Cady. McGraw-Hill Book Co., New York, N. Y. THIS JOURNAL, **35**, 495 (1913).

(86) "Chemistry of Monosaccharides and Polysaccharides," by Hans Pringsheim. McGraw-Hill Book Co., New York, N. Y. *Ind. Eng. Chem.*, **25**, 473 (1933).

PATENT

(87) Crystal Violet, with H. L. Trumbull. U. S. Patent 1,402,195 (1922).

IN MEMORIAM

(88) Memorial to Jesse E. Day, *Ind. Eng. Chem.*, *News Ed.*, **13**, 230 (1935).

(89) Memorial to William McPherson, THIS JOURNAL, **74**, 859 (1952).

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Kinetics of the Dissociation of Weak Acids and Bases—Application of Polarography and Voltammetry at Constant Current

BY PAUL DELAHAY AND WOLF VIELSTICH

RECEIVED MAY 6, 1955

The kinetics of dissociation of weak acids and bases can be studied quantitatively from current–potential or potential–time curves for electrode reactions in poorly buffered solution. The nature of the substance being reduced or oxidized is rather immaterial, but the electrode reaction must involve hydrogen or hydroxyl ions. The weak electrolyte whose kinetics of dissociation can be studied by this method need not be reducible or oxidizable. A quantitative treatment is given for polarography and voltammetry at constant current, and the two methods are compared. Application is made to formic and acetic acids, and rate constants for dissociation (k_d and ionic recombination (k_r) in 50–50 water-ethanol mixture are at 25°: $k_d = 5.5 \times 10^4$ sec.$^{-1}$ and $k_r = 10^9$ l. mole^{-1} sec.$^{-1}$ for formic acid; $k_d = 2.9 \times 10^5$ sec.$^{-1}$ and $k_r = 9 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$ for acetic acid.

Electrochemical methods have been applied during the last decade to the kinetic study of chemical reactions coupled with electron transfer processes. Such investigations were pioneered in polarography by Brdicka and collaborators, and applications have been extended to some other electrochemical methods such as electrolysis with superimposed alternating voltage (Gerischer) and voltammetry at constant current (Gierst and Juliard, Delahay and Berzins). This material already has been reviewed in some detail.[1] Ionic recombination reactions have been studied by polarography for the particular case of reducible weak acids whose anion yields a distinct wave from that of the undissociated acid. *The more general case in which the weak acid or base is not necessarily reducible or oxidizable is considered here, and a method for the kinetic study of dissociation is described.* Comparison is also made with some results obtained by other methods recently developed for the study of fast ionic recombination processes.[2–4]

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(1) P. Delahay, "New Instrumental Methods in Electrochemistry—Theory, Instrumentation, and Applications in Analytical and Physical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1954; see Chapters 5, 7 and 8.

(2) (a) M. Eigen, *Z. physik. Chem.*, *N.F.*, **1**, 176 (1954); *Discs. Faraday Soc.*, **17**, 194 (1954); (b) M. Eigen and J. Schoen, *Z. physik. Chem.*, *N.F.*, **3**, 126 (1955). See also D. A. Bies, *J. Chem. Phys.*, **23**, 428 (1955).

(3) (a) R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953); (b) R. G. Pearson, *Discs. Faraday Soc.*, **17**, 187 (1954).

(4) (a) A. Weller, *Z. Elektrochem.*, **56**, 663 (1952); (b) A. Weller, *Z. physik. Chem.*, *N.F.*, **3**, 238 (1955).

Polarography

The half-wave potential of reversible waves for electrode reactions involving hydrogen ions is pH dependent.[5] This is quite often—but not always—the case for irreversible reactions involving hydrogen ions. When the supporting electrolyte is well buffered, a single wave is obtained provided that only one electrode reaction occurs. However, two waves can be observed in poorly buffered solution, as was shown conclusively by Rüetschi and Trümpler.[6] If the pH is adjusted with a strong acid at low concentration, the height of the first wave is controlled by the rate of diffusion of hydrogen ions toward the electrode. This is the case which was treated theoretically by Rüetschi and Trümpler. With a buffer, the rate of dissociation of the weak electrolyte of the buffer—or the rate of ionic recombination of the buffer constituents—must be considered when diffusion of reactants to the electrode is not entirely rate controlling. Application is made below to the study of the kinetics of weak electrolyte dissociation. The case of weak acids will be considered, but the treatment readily could be extended to weak bases.

The limiting current for processes controlled by a first-order chemical reaction and by linear diffusion of the reactants was derived by Koutecky and Brdicka.[7] Koutecky also treated this problem for diffusion at the dropping mercury electrode for the case in which the diffusion coefficients of the species involved in the chemical process either are the same[8] or are different.[9] The latter treatment will be applied here.

The average current during drop life is

$$\bar{i} = 6.07\, n M^{2/3} t^{1/6} (C^0_{\mathrm{H}^+} + C^0_{\mathrm{HA}}) D^{1/2} \frac{0.87 \dfrac{D}{D_{\mathrm{HA}}}\left(\dfrac{D_{\mathrm{H}^+}}{D_{\mathrm{HA}}}\right)^{1/2}\left(\dfrac{k_{\mathrm{d}}tK}{C_{\mathrm{A}^-}}\right)^{1/2}}{1 + 0.87 \dfrac{D}{D_{\mathrm{HA}}}\left(\dfrac{D_{\mathrm{H}^+}}{D_{\mathrm{HA}}}\right)^{1/2}\left(\dfrac{k_{\mathrm{d}}tK}{C_{\mathrm{A}^-}}\right)^{1/2}} \qquad (1)$$

where $\bar{i}$ is in microamperes, n is the number of electrons involved in the electrode reaction ($n = 1$ here), m the rate of flow of mercury in mg. sec.$^{-1}$, (C°)'s the concentrations in millimole l.$^{-1}$, t the drop time in sec., K the dissociation constant of the weak acid, k_{d} the rate constant for the dissociation of the weak acid, and D is defined by

$$D = \frac{D_{\mathrm{H}^+} + C_{\mathrm{A}^-} D_{\mathrm{HA}}/K}{1 + C_{\mathrm{A}^-}/K} \qquad (2)$$

where D_{H^+} and D_{HA} are the diffusion coefficients of H^+ and HA.

Equation 1 is valid provided that dissociation is a pseudo-first-order process, *i.e.*, that a large excess of anions is present. It is seen that equation 1 reduces to the Ilkovic equation when $(k_{\mathrm{d}}tK/C_{\mathrm{A}^-})^{1/2}$ is large enough. The upper value of $(k_{\mathrm{d}}tK/C_{\mathrm{A}^-})^{1/2}$ for which the kinetics of dissociation can still be studied quantitatively can be determined by prescribing the condition $\bar{i} = 0.9\ \bar{i}_{\mathrm{d}}$, where $\bar{i}_{\mathrm{d}}$ is the average diffusion current calculated from the Ilkovic equation. A less stringent condition is not advisable because of the uncertainty on D and the complex nature of the mass transfer process at the dropping mercury electrode. Thus

$$\left(\frac{k_{\mathrm{d}}tK}{C_{\mathrm{A}^-}}\right)^{1/2} \leqslant 10 \qquad (3)$$

By introducing the representative value $t = 4$ sec. and the rate constant k_{r} for the recombination of H^+ and A^- one deduces from (3)

$$\frac{Kk_{\mathrm{r}}^{1/2}}{C_{\mathrm{A}^-}^{1/2}} \leqslant 5 \text{ sec.}^{-1/2} \qquad (4)$$

For instance if $k_{\mathrm{r}} = 10^{11}$ l. mole^{-1} sec.$^{-1}$ (see Discussion of Results), and $C_{\mathrm{A}^-} = 1$ mole l.$^{-1}$, condition (4) is satisfied for $K < 10^{-5}$ mole l. Condition (4) is less stringent for voltammetry at constant current as will now be shown.

Voltammetry at Constant Current

Application of voltammetry at constant current to the study of chemical reactions coupled with electron transfer processes was first made by Gierst and Juliard.[10] A quantitative treatment was developed in this Laboratory,[11] and applications to various types of reactions recently were reviewed.[12] Application to the kinetic study of the dissociation of $\mathrm{Cd(CN)_4^{--}}$ was made recently by Gerischer.[13] The transition time τ_{k} for an electrode process with control by linear diffusion and a first-order chemical reaction (here the pseudo-first-order dissociation of a weak acid in presence of a large excess of anions) is such that[14]

$$i_0\tau_{\mathrm{k}}^{1/2} = i_0\tau_{\mathrm{d}}^{1/2} - \frac{\pi^{1/2}C_{\mathrm{A}^-}^{1/2}}{2Kk_{\mathrm{r}}^{1/2}}\, i_0 \qquad (5)$$

where i_0 is the current density. There τ_{d} is the transition time which would be obtained if the chemical process preceding electron transfer were so fast as to preclude any kinetic effect. Since $i_0\tau_{\mathrm{d}}^{1/2}$ is independent of current density, $i_0\tau_{\mathrm{k}}^{1/2}$ varies linearly with i_0, and the rate constant k_{r} can be evaluated from the slope of the resulting plot. Equation 5 does not hold when $i_0\tau_{\mathrm{k}}^{1/2} << i_0\tau_{\mathrm{d}}^{1/2}$, but such extreme conditions need not be considered here. Equation 5 was derived by using a common value for the diffusion coefficients D_{H^+} and D_{HA}. Because of the uncertainty in the graphic determination of transition times, a more refined treatment, which would involve rather cumbersome algebra, was not developed.

Since transition times as short as 10^{-3} second can be measured without serious interference by the charging of the double layer,[10] one deduces from (5) the condition

$$\frac{Kk_{\mathrm{r}}^{1/2}}{C_{\mathrm{A}^-}^{1/2}} \leqslant 500 \text{ sec.}^{-1/2} \qquad (6)$$

by setting $i_0\tau_{\mathrm{k}}^{1/2} \leqslant 0.9 i_0\tau_{\mathrm{d}}^{1/2}$. This condition is somewhat more favorable than in polarography (compare with 3). Furthermore, the diffusion coefficient of HA and H^+ need not be known since the value of k_{r} is deduced from the slope of the plot of $i_0\tau_{\mathrm{k}}^{1/2}$ against i_0.

Experimental

Application of the constant current method was made to acetic and formic acid in 50-50 water-ethanol mixtures.

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[5] I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1954, p. 246.

[6] P. Rüetschi and G. Trümpler, *Helv. Chim. Acta*, **35**, 1021, 1486, 1957 (1952).

[7] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

[8] J. Koutecky, *ibid.*, **18**, 311 (1953).

[9] J. Koutecky, *ibid.*, **19**, 857 (1954).

[10] (a) L. Gierst and A. Juliard, "Int. Comm. Electrochem. Therm. Kin.," Proc. 2nd Meeting, Tamburini, Milan, 1951, pp. 117, 279; (b) *J. Phys. Chem.* **57**, 701 (1953).

[11] For details, see ref. 1, pp. 179–216.

[12] P. Delahay, *Discs. Faraday Soc.*, **17**, 205 (1954).

[13] H. Gerischer, *Z. physik. Chem.*, *N.F.*, **2**, 79 (1954).

[14] P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

Azobenzene previously used by Rüetschi and Trümpler[6] was the reducible substance. The cell previously described[12] was utilized, and a slightly modified version of the instrument already described[15] was used. Experimental procedures generally followed standard practice of polarography.

The dissociation constants of formic and acetic acid in the 50-50 water-ethanol mixtures were determined by measuring with a glass electrode (Beckman *p*H meter model G) the *p*H of mixtures of acid and salt of varied composition. No correction for the presence of alcohol was made since the accuracy of the kinetic data did not justify a very precise determination of the dissociation constants. The ionic strength was adjusted approximately at 1 mole l.$^{-1}$ with potassium chloride.

Discussion of Results

Potential–time curves for the acetate buffer of *p*H 7.4 are shown in Fig. 1 for three current densities. The transition time τ_k from A to B is partially controlled by the kinetics of dissociation of acetic acid and water. However, the contribution of the latter substance can be neglected. At potentials more cathodic than point B the concentration of acetic acid is equal to zero at the electrode surface, and water is the main source of hydrogen ions. The concentration of azobenzene at the electrode surface drops to zero around point C, and the potential then varies to cathodic values at which the supporting electrolyte is reduced.

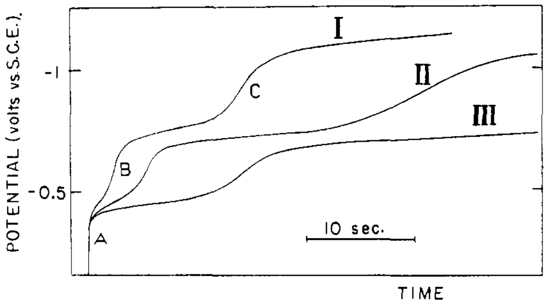

Fig. 1.—Potential–time curves for 2 × 10^{-3} molar azobenzene in acetate buffer of *p*H 7.4 in 50-50 water–ethanol mixture 6 × 10^{-4} molar in acetic acid and 5 × 10^{-2} molar in sodium acetate, current densities, I, 250; II, 177; and III, 106 microamp. cm.$^{-2}$. Ionic strength was adjusted at 1 mole l.$^{-1}$ with potassium chloride.

Values of the product $i_0\tau_k^{1/2}$ are plotted against current density in Fig. 2 for different buffers. Lines are shifted so that the intercepts at $i_0 = 0$ coincide. Note that straight lines $i_0\tau_k^{1/2}$ against i_0 are obtained as expected from equation 5. The influence of dissociation of acetic acid becomes more pronounced as the acetate ion concentration increases, *i.e.*, as the rate of recombination of ions H^+ and A^- increases. Diffusion control is observed for line 1 which is essentially horizontal. These data were collected with different concentrations of azobenzene. However, this is unimportant: the transition time for the first step is independent of the azobenzene concentration provided that a sufficient amount of this substance is present to have partial control by kinetics of weak acid dissociation.

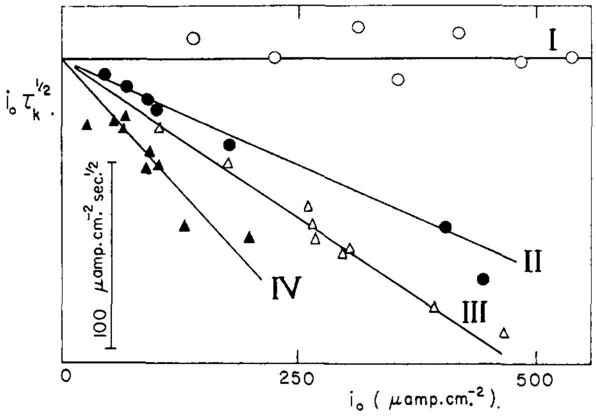

Fig. 2.—Variations of $i_0\tau_k^{1/2}$ with current density for azobenzene in acetate buffers of varied *p*H in 50-50 water–ethanol mixture; azobenzene concentrations: 2 (I), 0.5 (II), 2 (III) and 1 (IV) m*M*; acetic acid concentrations: 2.5 (I), 0.2 (II), 0.6 (III) and 0.4 (IV) m*M*; sodium acetate concentrations: 0.05 (I), 0.0125 (II), 0.05 (III) and 0.088 (IV) *M*. Ordinates at $i_0 = 0$: 885 (I), 175 (II), 430 (III) and 191 (IV) micro-amp. cm.$^{-2}$ sec.$^{1/2}$. Ionic strength adjusted at 1 mole l.$^{-1}$ with potassium chloride.

Similar results were obtained for formic acid. The results for this acid and for acetic acid are summarized in Fig. 3 in which the slope of the diagram $i_0\tau_k^{1/2}$ *vs.* i_0 is plotted against the square root of the anion concentration. A straight line is obtained as is to be expected from equation 5. The rate constants deduced from this diagram are as follows (25°) for formic acid: $k_d = 5.5 \times 10^4$ sec.$^{-1}$, $k_r = 10^9$ l. mole^{-1} sec.$^{-1}$; for acetic acid, $k_d = 2.9 \times 10^5$ sec.$^{-1}$, $k_r = 9 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$. The values of the dissociation constants for the 50-50 water–ethanol solvent, $K = 5.5 \times 10^{-5}$ mole l.$^{-1}$ for formic acid and $K = 3.3 \times 10^{-6}$ mole l.$^{-1}$ for acetic acid, were used in the computation of the rate constants.[16] The relative error on the *k*'s is smaller than 50%. The above *k*'s for acetic acid are of the same order of magnitude as the data recently reported by Eigen and Schoen.[2b] These authors obtained from study of the second Wien effect for aqueous solutions of acetic acid: $k_d = 8 \times 10^5$ sec.$^{-1}$ and $k_r = 4.5 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$.

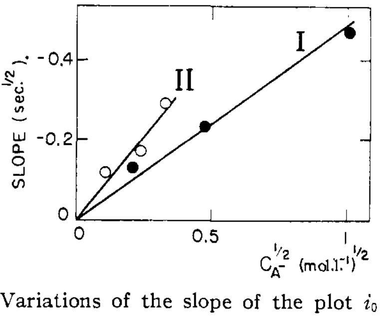

Fig. 3.—Variations of the slope of the plot $i_0\tau_k^{1/2}$ *vs.* i_0 with the square root of anion concentration: I, formic acid; II, acetic acid.

The above data on k_r for acetic acid are not too different from the approximate value $k_r = 10^{11}$ l. mole^{-1} sec.$^{-1}$ one deduces from Onsager's treat-

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[15] P. Delahay and C. C. Mattax, THIS JOURNAL, **76**, 876 (1954).

[16] See also the precise determinations of *K* by E. Grunwald and B. J. Berkowitz, *ibid.*, **73**, 4939 (1951).

ment.[17] However, the experimental k_r for formic acid is appreciably lower than the above calculated value. The possibility of the formation of a partially covalent bond between H^+ and A^- is not taken into account in Onsager's treatment, and this possibly accounts for the discrepancy. Much lower values for k_r than those obtained in this work have been obtained[3,6] by various methods. In some of these methods there may be some uncertainty as to whether experimental values of k_r correspond to the formation of neutral molecules or ion pairs.[18]

The rate constants k_d obtained by polarography or voltammetry at constant current are somewhat too high because of the influence of electrical field on the rate of dissociation of the acid molecules (Onsager).[17] The chemical reaction essentially occurs in a layer whose thickness is[19]

$$\mu = D^{1/2}/k_r^{1/2} \qquad (7)$$

The concept of reaction layer is somewhat arbitrary although statistical interpretation can be given for μ.[20] For $D = 10^{-5}$ cm. sec.$^{-1}$, $k_r = 10^{10}$ l. mole^{-1} sec.$^{-1}$, one has $\mu = 3 \times 10^{-8}$ cm. This is the order of magnitude of the Helmholtz double layer thickness. There the electrical field is very high,[21] perhaps 10^6 volts cm.$^{-1}$, and the resulting increase in k_d is appreciable. According to Onsager[17] (see also Pearson[3]) one has

$$k_d = k^0_d\,(1 + ed\,|\phi\,|/kT) \qquad (8)$$

where k and T have their usual significance, k^0_d is the rate constant for dissociation for $\phi = 0$, e is the charge on the ion, ϕ is the field intensity, and d is the maximum distance of separation of the two ions in the ion pair. One has $d \approx 3.5\ 10^{-8}$ cm. at 25° for water.[3] For $\phi = 10^6$ volts cm.$^{-1}$ one has at 25° $k_d/k^0_d = 39$ as an order of magnitude of the error resulting from the electric field effect. Such a calculation is very approximate because the electrical field in the vicinity of the electrode is not homogeneous and is not known with any degree of certainty. Furthermore the introduction of μ leads to additional uncertainty, and *the above calculation only indicates that the field effect is not entirely negligible in this method.* Another difficulty results from the application of Fick's equation when μ is of molecular dimension.[22]

Conclusion

The kinetics of dissociation of weak acids or bases can be studied in a simple manner by polarography or voltammetry at constant current. The latter method is somewhat more advantageous than the former especially when the acid or base is not very weak ($K > 10^{-5}$ mole l.$^{-1}$). Application to physical organic chemistry might be of interest.

Acknowledgment.—The support of the Office of Naval Research is gladly acknowledged.

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[17] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1943). See also H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, pp. 67, 110, 113. See also P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

[18] *Discs. Faraday Soc.*, **17**, 230 (1954).

[19] See ref. 1, p. 202.

[20] (a) K. Wiesner, *Chem. Listy*, **41**, 6 (1947); (b) E. F. Orleman and D. M. H. Kern, THIS JOURNAL, **75**, 3058 (1953).

[21] D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

[22] D. M. H. Kern, THIS JOURNAL, **75**, 2473 (1953).

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[CONTRACT NO. W-7405-ENG-48, UNIVERSITY OF CALIFORNIA, RADIATION LABORATORY, LIVERMORE SITE]

The Decomposition of Tetraalkylammonium Amides and Tetraethylammonium in Liquid Ammonia. The Preparation of a Substituted Ammonium Amide

BY WILLIAM L. JOLLY

RECEIVED FEBRUARY 18, 1955

The over-all decomposition of tetraethylammonium in liquid ammonia involves the formation of triethylamine, hydrogen, ethylene and ethane. The hydrogen comes from the reaction of electrons with the solvent to form amide ions; the triethylamine and ethylene are formed from the reaction between amide ions and tetraethylammonium ions, and the ethane is produced by the hydrogenation of the ethylene. The reactions of tetraalkylammonium ions with amide ions have been studied; it has been shown that the tetraethylammonium ion is stable in the presence of the diphenylamide ion or the anilide ion. Tetraethylammonium diphenylamide has been prepared and characterized.

The work of Schlubach and Ballauf[1,2] on liquid ammonia solutions of tetraethylammonium led those investigators to conclusions which are entirely opposed to modern theories of the nature of electron-ammonia solutions and theories of the attack of bases on quaternary ammonium compounds. Consequently, the present investigation was begun.

It soon became apparent that one must assume tetraethylammonium to be practically completely ionized in liquid ammonia as tetraethylammonium ions and electrons.[3] Electrons are known to react slowly (in the absence of a catalyst) with the solvent to give colorless amide ions and hydrogen

$$e^- + NH_3 = NH_2^- + {}^1/{}_2H_2 \qquad (1)$$

Therefore, the first step of the investigation was the study of the reaction of amide ions with tetraethylammonium ions. It was easily demonstrated that the products include triethylamine and ethylene

$$Et_4N^+ + NH_2^- = NH_3 + Et_3N + C_2H_4 \qquad (2)$$

Equation 2 represents a typical reaction of a base with a quaternary aliphatic ammonium ion.[4] In this case, the base is strong enough to cause reaction at −75°, as evidenced by the liberation of ethylene gas.[5]

However, in the decomposition of tetraethylam-

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[1] H. H. Schlubach, *Ber.*, **53B**, 1689 (1920).

[2] H. H. Schlubach and F. Ballauf, *ibid.*, **54B**, 2811 (1921).

[3] H. A. Laitinen and C. J. Nyman [THIS JOURNAL, **70**, 3002 (1948)], using a platinum cathode, have shown that the potential of electron dissolution is the same for solutions of alkali metal iodides and tetraalkylammonium iodides.

[4] S. W. Kantor and C. R. Hauser [*ibid.*, **73**, 4122 (1951)] and Thomson and Stevens [*J. Chem. Soc.*, 1932 (1932)] have used sodium amide to rearrange quaternary ammonium ions.

[5] It was also shown that the tetra-*n*-propylammonium and tetra-*n*-butylammonium ions react with amide ions in liquid ammonia to give the corresponding trialkylamines and 1-olefins. The propylene and 1-butene do not effervesce from liquid ammonia as readily as does ethylene, however, probably because of the higher solubilities of the former olefins.