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°_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° $k_d/k^\circ_d = 39$ 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.

---

[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).

BATON ROUGE 3, LA.

[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-

---

[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.

monium solutions, only a part of the ethylene escapes from the solution. Some of it is reduced to ethane, since it is formed *in situ* in a solution of electrons. As a result, the volatile decomposition products consist of hydrogen, ethylene and ethane, the relative amounts depending on the fraction of ethylene hydrogenated. Reaction (2) and the side reaction leading to ethane were fast enough, in this investigation, to appear simultaneous with eq. 1. However, it is possible that in Schlubach and Ballauf's[2] cold solutions of "colorless tetraethylammonium," there existed in reality a finite concentration of tetraethylammonium amide.

The above results made it apparent that it would be impossible to prepare solid tetraethylammonium amide.[6] It was considered of interest to find a substituted amide ion sufficiently weak as a base to permit the existence of the tetraethylammonium salt. The diphenylamide ion, $N(C_6H_5)_2^-$, is one such ion; not only are liquid ammonia solutions of tetraethylammonium diphenylamide stable, but the solid salt is stable at room temperature. Tetraethylammonium diphenylamide is a yellow solid that reacts vigorously with water to give diphenylamine and a solution of tetraethylammonium hydroxide. The material becomes wet and green when exposed to the air. It is only slightly soluble in liquid ammonia and may be prepared from this solvent by the metathetic reaction between sodium diphenylamide and tetraethylammonium bromide. When heated to 70° or higher, it decomposes into ethylene, triethylamine and diphenylamine.

An attempt to prepare tetramethylammonium diphenylamide by a similar metathesis failed, probably because of its greater solubility in ammonia. Attempts to prepare tetrapropylammonium diphenylamide by the reaction between tetrapropylammonium iodide and sodium diphenylamide yielded only very impure products, highly contaminated with tetrapropylammonium iodide.

It was shown that the diethylamide ion, NEt_2^-, is a strong enough base to decompose the tetraethylammonium ion in liquid ammonia. However, the anilide ion, $NH(C_6H_5)^-$, is a weak enough base that solutions of tetraethylammonium anilide in ammonia are stable at the boiling point.

Experimental

Reaction between KNH_2 and Et_4NBr.—Three and one-tenth grams of potassium amide was added to a suspension of 10 g. of tetraethylammonium bromide in about 150 ml. of ammonia at −72°. Effervescence immediately occurred. The evolved gas was separated from ammonia with a dilute acid scrubber and was shown to decolorize bromine water. After the ammonia boiled away, the liquid remaining in the reaction vessel was distilled out and its boiling point was measured with a micro-boiling point apparatus; b.p. found, 91° (uncor.); b.p. of triethylamine,[7] 89.5°.

In another experiment, 1.8 g. of tetraethylammonium bromide was added to a solution of 0.4 g. of potassium amide in 100 ml. of liquid ammonia at −75°. Vigorous effervescence occurred immediately. The evolved gas, along with some ammonia, was condensed and freed of ammonia by distillation from −125 to −195°; vapor pressure at −119°, found 27 cm.; literature[7] value for ethylene, 28 cm.

Reactions between KNH_2 and $(n\text{-}Pr)_4NI$ or $(n\text{-}Bu)_4NI$.—Eight-tenths gram of $(n\text{-}Pr)_4NI$ was added to a solution of 0.10 g. of potassium amide in 40 ml. of liquid ammonia at −70° with no apparent reaction. The solution showed no effervescence while warming to the boiling point. The gas evolved from the boiling solution was freed of ammonia by passage through 400 ml. of 2.4 *M* hydrochloric acid. When the hydrochloric acid was neutralized, approximately 25 cc. of gas had collected which, after a simple fractionation, was identified as propylene (vapor pressure of propylene at −104°, found 1.6 cm.; literature[7] 2.0 cm.). After evaporating all the ammonia from the reaction tube, a small amount of liquid was vacuum distilled from the residue and was identified as tri-*n*-propylamine (boiling point of tri-*n*-propylamine, found 155–157°; literature[7] 156°). An analogous experiment was carried out using tetra-*n*-butylammonium iodide. Two cc. of 1-butene (vapor pressure at −64°, found 3.55 cm.; literature[7] 3.8 cm.) and a small amount of tri-*n*-butylamine (b.p. found, 210°; literature[7] 214°) were isolated.

The Decomposition of Et_4N.—Eleven grams of tetraethylammonium bromide was suspended in about 100 ml. of liquid ammonia at −60°, and 1.2 g. of sodium metal was added. The suspension was swirled occasionally and allowed to warm up slowly (over a period of one hour) to −36°, and then held at this temperature. During this time a stream of argon was passed, successively, over the solution, through two dilute sulfuric acid washing bottles, and through a bromine water washing bottle. Some effervescence started in the ammonia suspension when the temperature reached −40°, and shortly thereafter the bromine water began to lose color. The decomposition was so slow, however, that a tiny crystal of ferric nitrate was added to accelerate the reaction. The solution then decolorized very quickly and two liquid phases (ammonia and triethylamine) remained.

A similar experiment was carried out using smaller amounts of sodium and tetraethylammonium bromide (0.06 and 1.34 g., respectively). The solution was allowed to boil and the evolved gases were scrubbed free of ammonia with 30% sulfuric acid. The remaining gases were then analyzed with a mass spectrometer and were found to consist of ethylene, ethane and hydrogen in the mole percentages 42.1, 56.8 and 1.0%. In another experiment, a solution of sodium and tetraethylammonium bromide in ammonia (0.13 g., 1.6 g. and 70 ml., respectively) was allowed to decompose at the boiling point, using a tiny crystal of ferric nitrate as catalyst. After scrubbing the gases with 2.4 *M* hydrochloric acid, they were analyzed mass spectrometrically and were found to consist of ethylene (62.6%), ethane (8.0%) and hydrogen (29.4%).

The gas analyses of the above two experiments lead to H/C ratios of 2.58 and 2.53, respectively, which are reasonably close to the theoretical ratio, 2.50, corresponding to complete reaction.

There remained the possibility that the acid scrubbing solutions catalyzed the hydrogenation of the ethylene. Hence, a solution of tetraethylammonium was decomposed and the gaseous products were freed of hydrogen and ammonia by fractionation in a vacuum system. The remaining gases were found by mass spectrometry to be 97.7% ethylene and 2.3% ethane.

Preparation of $Et_4NN(C_6H_5)_2$.—After several preliminary experiments (which proved that $Et_4NN(C_6H_5)_2$ is reasonably stable at room temperature), the following typical procedure was found to be satisfactory for preparing the compound. About 150 ml. of liquid ammonia was drawn from a cylinder into a small unsilvered dewar. Just enough small pieces of sodium were added to make a permanently blue solution. Another piece of sodium (0.19 g.) and 1.4 g. of diphenylamine were then added. After complete reaction, the greenish-yellow solution was siphon-filtered into a tube with a sintered-glass bottom which held 1.3 g. of tetraethylammonium bromide. During the siphon-filtration and for several minutes thereafter, a slow stream of argon was passed up through the filter disk. This served to keep the solution from passing through the filter disk, stirred the solution, and flushed air out of the tube. A stopcock immediately below the filter was then closed and the tube was connected to a vacuum manifold. After flushing the system free of air, the lower stopcock was then opened momentarily to allow the solution to pass through the filter. The material remaining on the filter was

---

(6) E. C. Franklin ["The Nitrogen System of Compounds," Reinhold Publ. Corp., New York, N. Y., 1935, p. 63] reported an unsuccessful attempt to prepare tetramethylammonium amide by the metathesis of tetramethylammonium chloride and potassium amide. The amide ion attacked the tetramethylammonium ion to form trimethylamine and methylamine.

(7) C. D. Hodgman, editor, "Handbook of Chemistry and Physics," 33rd Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1951.

then washed with liquid ammonia several times. After the final washing, the system was pumped down to a pressure of 10^{-2} mm. and one atmosphere of argon was admitted. The tube was quickly transferred to an argon-filled dry box and the product was transferred to small screw-cap bottles (1.0 g. yield).

Analysis of $Et_4NN(C_6H_5)_2$.—Samples were weighed out in the argon dry box into erlenmeyer flasks and, after removing from the dry box, about 50 ml. of water was added (while the samples were under a blanket of argon). The material immediately hydrolyzed and left a suspension of white diphenylamine. The solutions were titrated with 0.1 *N* hydrochloric acid to determine the amount of tetraethylammonium hydroxide, and the precipitate of diphenylamine was filtered off and weighed. Typical analysis: Et_4N^+ calcd., 43.6%; found, 41.2, 40.1%. $N(C_6H_5)_2^-$ calcd., 56.4%; found, 57.4, 59.9%. The above method of analysis does not completely distinguish between $Et_4NN(C_6H_5)_2$ and $NaN(C_6H_5)_2$, since both materials hydrolyze to give a suspension of diphenylamine in a basic solution. So two separate samples were analyzed for sodium by igniting to dryness with sulfuric acid and were found to contain only 0.08 and 0.1% sodium. Another sample (containing about 15% diphenylamine impurity) was analyzed for Et_4N^+ by running a Kjeldahl analysis on the aqueous solution remaining after hydrolysis and titration. Et_4N^+ calcd., 43.6%; found by Kjeldahl, 34.3%; found by titration, 37.3%. No preparation ever analyzed better than 94% pure, diphenylamine being the usual impurity.

Stability of $Et_4NN(C_6H_5)_2$.—When $Et_4NN(C_6H_5)_2$ is gradually heated in an evacuated closed system, decomposition (as evidenced by gas evolution) starts at 75–80°. At 100°, decomposition is very rapid and the material melts and effervesces. The gas evolved from one sample was analyzed mass spectrometrically (98% ethylene was found); the amount of gas evolved was approximately 100% of theory (accounting for the impurities present).

When the material is held over a flame, it quickly ignites, leaving a gummy residue which is slightly more difficult to ignite. Dry air causes the material to turn dark green in one day, and after one week, a dark viscous liquid remains. This residue dissolves in organic solvents to give colored solutions, the color apparently depending on the time of exposure to air. Because of this reactivity to air, it is necessary to store $Et_4NN(C_6H_5)_2$ in sealed glass vials or tight-fitting screw-cap bottles.

Acknowledgments.—The author is grateful to Dr. Donald R. Bomberger and Mr. Antoine A. Franke for many of the chemical analyses. Mr. Herbert X. Di Grazia and Mrs. Bobby Mohler carried out the mass spectrometric gas analyses. The author also wishes to thank Dr. Eugene R. Bissell for his helpful discussions. This work was sponsored by the U. S. Atomic Energy Commission.

LIVERMORE, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Effect of Solutes on the Molecular Yields in the Radiolysis of Aqueous Solutions[1]

BY HAROLD A. SCHWARZ

RECEIVED APRIL 7, 1955

The molecular H_2 yield produced by γ-rays in KNO_2 and $CuSO_4$ solutions is found to decrease as the solute concentration is increased in the range of 10^{-5} to 1 molar. In $CuSO_4$ solutions, the Cu^{++} ion is the active species. Comparison of these data with published data on the effect of H_2O_2 on the H_2 yield and the effect of KBr and KCl on the molecular H_2O_2 yield shows that all of these yields *vs.* concentration curves coincide when the solute concentration is multiplied by a characteristic normalization constant. It is concluded that the mechanisms for formation of H_2 and H_2O_2 are similar as has been proposed by other authors. In the case of H_2 yields, the normalization factors are in the same ratio as the rate constants for reaction of H atoms with the solute wherever these are known. All of these results are consistent with the radical diffusion model in which H_2 and H_2O_2 are formed by combination of H and OH radicals as they diffuse out of a spur. A simple, approximate mathematical treatment of this model is given.

In the radiolysis of aqueous solutions by γ-rays, yields of H_2 and H_2O_2, called the molecular yields, are produced which are relatively independent of the nature of the solute.[2,3] Allen has ascribed these yields to the combination reactions of H and OH radicals as they diffuse away from the "hot spots" or "spurs" in which they are formed.[4] Samuels and Magee have attempted to calculate the magnitude of the yields to be expected from a radical diffusion model and find the model in agreement with the observed yields.[5]

On the basis of such a model, solutes that react with H atoms would be expected to lower the yield of H_2, and those that react with OH radicals would lower the H_2O_2 yield. The effect of solutes on the yield of H_2O_2 has been studied by several authors.[6–9] Hochanadel and Ghormley have studied the effect of H_2O_2 on the H_2 yield.[10] In the present paper, studies of the effect of KNO_2 and $CuSO_4$ on the H_2 yield are reported along with certain correlations that can be found among existing data.

Experimental

The preparation and analysis of the samples has been described elsewhere.[3] KNO_2 solutions were also examined for NO. A small known quantity of O_2 was added to the product gases in the analysis system. The pressure was noted before and several times after the O_2 was added. In the cases of the more concentrated KNO_2 solutions, a gas was present which spontaneously reacted with O_2 and froze out on liquid N_2. This gas was presumed to be NO.

Solutions were prepared with a known concentration of solute and then deaerated by boiling under vacuum. In most cases, portions of the solution were analyzed after deaeration. The concentration of the solute increased by approximately 5% during deaeration.

Results

The hydrogen yields, solution compositions and total doses are given in Tables I, II and III. All *G*

---

[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

[3] H. A. Schwarz, J. P. Losee and A. O. Allen, *ibid.*, **76**, 4693 (1954).

[4] A. O. Allen, *Disc. Faraday Soc.*, **12**, 79 (1952).

[5] A. H. Samuels and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

[6] T. J. Sworski, THIS JOURNAL, **76**, 4687 (1954); *Radiation Research*, **2**, 26 (1955).

[7] F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.*, **49**, 1011 (1953).

[8] H. A. Schwarz and A. O. Allen, THIS JOURNAL, **77**, 1324 (1955).

[9] A. O. Allen and R. Holroyd, 127th National A.C.S. Meeting, 1955.

[10] J. A. Ghormley and C. J. Hochanadel, Radiation Research Society meeting, New York, N. Y., May 16, 1955.