question show unusual adsorptive properties, *i.e.*, the electrolytes form strongly adsorbable complexes or the resin shows unusual solvent properties for the non-electrolytes or weak acids.

Acknowledgment.—The authors are indebted to Mrs. L. W. Magnusson, Jr., and Miss Zella Bonner for valuable technical assistance.

OAK RIDGE NATIONAL LABORATORY
CHEMISTRY DIVISION
OAK RIDGE, TENN.

The Reaction of Lithium Amide with Diborane

BY GEORGE W. SCHAEFFER AND LOUIS J. BASILE[1]

RECEIVED JULY 29, 1954

Diborane reacts with an ether slurry of lithium amide to give lithium borohydride and polymeric aminoborine.

$$B_2H_6 + LiNH_2 = LiBH_4 + BH_2NH_2 \qquad (1)$$

When there is an excess of diborane, the reaction proceeds rapidly and completely, the excess diborane is recovered unchanged, all of the lithium is found as the ether-soluble borohydride, and all of the nitrogen remains as an ether-insoluble material possessing the empirical formula NH_2BH_2.

No appreciable reaction takes place between solid lithium amide and diborane gas but if diethyl ether[2] is added, the reaction proceeds smoothly and rapidly, even at −64°. The need of an ether medium is similar to its necessity in the reaction between diborane and lithium hydride to give lithium borohydride. Using finely ground lithium amide the reaction was usually complete in less than one-half hour; for somewhat coarser material, the time of reaction was considerably longer. If care is not taken to moderate the reaction, significant amounts of hydrogen are produced or if lithium amide is taken in considerable excess, all of the diborane reacts and a large amount of hydrogen is produced. It appears from the observed pressure changes that the initial reaction between the amide and diborane is unchanged and that the hydrogen probably arises from further reaction between the products of the initial reaction and the excess amide. These hydrogen-producing reactions have not been investigated.

Experimental

Materials.—Commercial lithium amide of 98% purity, as determined by the ammonia produced on hydrolysis, was used. Diborane was prepared from lithium hydride and diethyl ether–boron fluoride.[3]

Reaction of Lithium Amide and Diborane.—A weighed sample of lithium amide was introduced through a side-arm into a reaction tube attached to the usual vacuum apparatus for the handling of condensable gases,[4] after which the side-arm was sealed and the reaction tube evacuated. Anhydrous ether and a measured volume of diborane were condensed onto the lithium amide. The reaction tube was so arranged that it could be sealed from the vacuum apparatus or could be made to connect to a manometer by means of which pressure changes could be followed.

After completion of the reaction, the hydrogen was measured and all other volatile products were transferred to the vacuum apparatus and carefully examined. The results of several experiments are given in Table I. The excess diborane in the amount recorded and pure diethyl ether were the only volatile substances detected. No nitrogen was found in the ether-soluble material. If the diborane was in excess (experiments 1 to 5), one mole reacted for each mole of lithium amide taken within the time needed (about one-half hour) to bring the reactor to room temperature. Extending the time of contact resulted in no further change (compare experiments 1 and 5). When the reaction mixture was brought to room temperature rapidly (experiments 6 and 7), considerable hydrogen was produced, probably because of localized heating which, under these conditions, would always occur during the initial phase of the reaction.

TABLE I

THE REACTION OF LITHIUM AMIDE WITH DIBORANE

Expt.	$LiNH_2$, mmoles	B_2H_6, mmoles	B_2H_6 consumed, mmoles	Time	H_2, cc.	$B_2H_6/LiNH_2$
1	9.7	17.7	8.5	1 hr.	Trace	0.88
2	4.77	8.17	4.33	1 da.	Trace	.91
3	3.57	6.52	3.53	1 da.	Trace	.99
4	6.30	13.4	6.21	1 da.	7	.99
5	9.68	14.3	9.60	7 da.	7	.99
6	8.03	12.2	7.36	1 da.	61	.92
7	9.15	13.4	8.08	3 hr.	67	.88
8	16.4	13.7	13.7	14 da.	188	
9	10.7	2.90	2.90	1 da.	34	
10	13.4	4.91	4.91	1 da.	43	

When the amide was in excess, all the diborane taken was consumed (experiments 8, 9 and 10), but considerable hydrogen was produced. By observation of the pressure changes during the reaction it was evident that hydrogen continued to evolve by a slower, but nevertheless rapid, reaction after the absorption of diborane was complete.

Identification of the Products.—In two experiments (1 and 2) under conditions which presumably resulted in a simple process, the non-volatile reaction products were extracted with diethyl ether, the product being divided into ether-soluble and ether-insoluble portions. The technique which was employed permitted complete recovery of the ether soluble material but only partial recovery of the ether-insoluble material. Analyses of the total ether-soluble material for boron and hydrolyzable hydrogen and of a portion of the insoluble material for boron and nitrogen are recorded in Table II. From these data it is evident that the ether-soluble material is lithium borohydride (boron to hydrogen ratio 1.0 to 3.8, theory 1.0 to 4.0) and that one mole of the borohydride is found for each mole of lithium amide taken (boron to lithium amide ratio 1.00 to 1.01). By difference, the ether-insoluble material should be BH_2NH_2 and this is confirmed by the boron to nitrogen ratio of 1.00 to 0.95 (theory 1.00 to 1.00) obtained by direct analysis.

TABLE II

ANALYSIS OF THE REACTION PRODUCTS

$LiNH_2$	Ether-soluble portion				Ether-insoluble portion		
taken, mmoles	H_2, meq.	HBO_2, meq.	B/H	Li/B	HBO_2	NH_2	B/N
	15.1	4.07	1:3.70		2.96	3.05	1:1.02
4.65	18.3	4.78	1:3.82	1:0.97	1.83	1.69	1:0.93
3.47	12.82	3.38	1:3.80	1:1.02	1.31	1.22	1:0.93

The identity of the ether-soluble product is confirmed by a further observation on the reaction product derived from 5.23 mmoles of lithium amide. Diethyl ether was added in portions, the equilibrium pressure being recorded after each addition. The plot of pressure against mole ratio of ether to the lithium amide originally taken was identical with that expected for 5.23 mmoles of lithium borohydride. The observed dissociation pressure between mole ratio of 0.54 and 0.92 was 9 to 12 mm. compared with 11.4 mm. for lithium

---

(1) Taken from a thesis submitted to the Graduate School of St. Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. Rapp, THIS JOURNAL, **75**, 199 (1953).

(3) H. I. Schlesinger, H. C. Brown, J. K. Gilbreath and J. S. Katz, *ibid.*, **75**, 195 (1953).

(4) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

borohydride monoetherate.[2,5] The inflection expected for the monoetherate at mole ratio 1.00 was observed between mole ratios 0.96 and 1.02.

Reaction at Reduced Temperature.—At −80° the reaction is slow, in one experiment 0.03 mole of diborane for each mole of lithium amide being absorbed in 12 hours, while under similar conditions but at −45°, the reaction is complete within several hours. At −65° the reaction appears to cease after absorption of approximately one-half mole of diborane, but whether this indicates a stepwise reaction or results from coating of the sample could not be determined, as duplication proved difficult.

Discussion

The simplicity of the stoichiometry and the absence of side reactions when the reaction is carried out under controlled conditions suggest a simple process. By analogy to the behavior of diborane toward lithium hydride to give lithium borohydride[2] it might be expected a borine group would add to an electron pair of the amide ion.

$$^1/_2B_2H_6 + LiNH_2 = LiH_3BNH_2 \qquad (2)$$

Displacement of the weak acid, aminoborine, by the stronger acid, borine, would then result in the products observed.

$$LiH_3BNH_2 + {}^1/_2B_2H_6 = LiBH_4 + BH_2NH_2 \qquad (3)$$

An alternate, but less probable, process which could lead to the observed products is the addition of a second borine to the product of reaction (2)

$$LiH_3BNH_2 + {}^1/_2B_2H_6 = LiBH_3NH_2BH_3 \qquad (4)$$

followed by the displacement of the weak acid, aminodiborane, by the stronger acid, borine

$$LiBH_3NH_2BH_3 + {}^1/_2B_2H_6 = LiBH_4 + B_2H_5NH_2 \qquad (5)$$

and the decomposition of the aminodiborane

$$B_2H_5NH_2 = BH_2NH_2 + {}^1/_2B_2H_6 \qquad (6)$$

Although every effort was made to detect the presence of aminodiborane, a fairly stable substance under the conditions of the reaction,[6] and to isolate the lithium salt $LiH_3BNH_2BH_3$, which by analogy to the corresponding sodium salt[7] $NaH_3BNH_2BH_3$ ought to be stable, no support for this alternate process could be obtained.

The reaction between lithium amide and diborane provides a convenient method for the preparation of polymeric aminoborine, a substance heretofore available only by the decomposition of aminodiborane.[8]

[5] T. Kolski, Master's Thesis, St. Louis University, January, 1954.

[6] G. W. Schaeffer and M. D. Adams, unpublished.

[7] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

[8] H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 2297 (1938).

ST. LOUIS UNIVERSITY
ST. LOUIS 4, MISSOURI

The Kinetics of Hydrolysis of Acetyl Chloride in Acetone–Water Mixtures

BY GEORGE ZIMMERMAN AND CHING YUAN

RECEIVED AUGUST 6, 1954

A number of careful studies of the kinetics of hydrolysis and alcoholysis of acid halides have been made recently[1-8]; in several instances for relatively low concentrations of water (or alcohol) in a non-reacting solvent, the reaction was second order with respect to water (or alcohol) and first order with respect to acid halide.[2,5,7] A termolecular mechanism has been proposed[2,5] and is consistent with the observed low activation enthalpies and entropies. Hudson and co-workers[1-3] have shown that several independent mechanisms are required to account for the kinetic behavior of benzoyl chloride hydrolysis over a wide range of water concentrations in several solvents. Using conductometric methods, we have measured the rate of hydrolysis of acetyl chloride dissolved in acetone containing 1 to 5% of water. The results seem to fit well into and to substantiate the above picture.

Experimental.—Acetyl chloride was purified carefully as recommended by Fieser,[9] and stored in a special buret in an atmosphere of dry nitrogen; from this the CH_3COCl could be added to dry acetone[10] in the absence of moisture or to the various acetone–water mixtures. The conductance cell used was a modified "pipet type" cell,[11] of 12 ml. volume and with a cell constant of 0.253 cm.$^{-1}$. A conventional a.c. bridge circuit[12] using a Leeds and Northrup 1000-cycle oscillator and a cathode ray oscilloscope as the current detector was employed. The cell had such a small capacitance that relatively little precision was to be gained by capacitance balancing. For a given run the acetone–water mixture was brought to bath temperature, approximately the desired amount of CH_3COCl was added and mixed (in about 8 seconds; zero time taken halfway through), the cell rinsed, filled, and mounted in the bath (in about 1 min.). The remaining mixture was sealed and kept in the bath for at least 24 hr., in order that the reaction proceed to completion. Part was then titrated with standard base to obtain the exact initial concentration of CH_3COCl, and part was used for an infinite-time conductance measurement. All runs were carried out with a sufficiently large ratio, concn. of H_2O/concn. of CH_3COCl, that first-order kinetics were observed over a wide range of reaction. For a given acetone–water mixture the dependence of conductance on the concentration of reaction products was found by measuring the conductance of a completely reacted solution at various dilutions (with the same water–acetone mixture). Actually, over the range of reaction studied in most runs, the conductance was so close to being a linear function of the concentration of products that it was assumed exactly so. In this case (for a first-order reaction) a plot of $\log(L_\infty - L_t)$ against t (L_t = measured conductance at time, t) should be a straight line with a slope of $k'/2.303$ (k' = pseudo first-order rate constant).[13]

Results.—Figure 1 shows $[\log (L_\infty - L_t) + 5]$ plotted against t for two typical runs and justifies to within 2–3% the assumptions made in the kinetic analysis. Table I summarizes data for the runs of interest; in a few cases (with smaller ex-

[1] D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 883, 888, 3352 (1953).

[2] B. L. Archer and R. F. Hudson, *ibid.*, 3259 (1950).

[3] R. F. Hudson and J. E. Wardill, *ibid.*, 1729 (1950).

[4] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 246 (1953).

[5] C. G. Swain, *ibid.*, **70**, 1124 (1948).

[6] C. G. Swain and S. D. Ross, *ibid.*, **68**, 658 (1946).

[7] A. A. Ashdown, *ibid.*, **52**, 268 (1930).

[8] See also, L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 189.

[9] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941.

[10] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford University Press, London, 1935.

[11] E. B. Millard, "Physical Chemistry for Colleges," 7th Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 261.

[12] F. Daniels, *et al.*, "Experimental Physical Chemistry," 4th Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 455.

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Chapt. 3.