Summary

The dipole moments of a number of bonds have been calculated from the moments of the molecules containing them and the structures of these molecules as indicated by electron diffraction or other information. A graphical comparison of the moments of single bonds with the electronegativities of the elements involved shows approximate consistency except for the bonds between carbon and larger atoms, which have moments apparently greatly increased by induction.

The moments of double and triple bonds are commonly increased by contributions from forms containing semipolar bonds. Somewhat mixed forms of semipolar bonds affected by resonance have moments between 2.4 and 3.5×10^{-18}, the values varying from compound to compound by no more than 0.8 because of resonance. Semipolar bonds have polarities intermediate between those of ordinary covalent bonds and those of electrovalent bonds.

PRINCETON, NEW JERSEY RECEIVED JULY 14, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of Heterogeneous Catalysis in Liquid Ammonia Solutions. I

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Introduction

Solutions of the alkali and alkaline earth metals in liquid ammonia are known to be relatively stable, existing for many hours without appreciable reaction between the metal and the solvent ammonia. Yet a slow reaction does occur, and earlier workers[2-4] with liquid ammonia as a solvent prepared the amides of sodium and potassium in this way. In some cases, days and even months were required for complete reaction. That the rate of the reaction between metals and liquid ammonia could be speeded up by the presence of other substances was first observed by Franklin,[5] who noticed that in tubes containing bits of asbestos fiber, the time for preparation of potassium amide was shortened appreciably. Other catalytic agents were tried and platinum black and oxides of iron were found to be especially effective. Franklin stated that a few milligrams of platinum black so speeded up the reaction that as much as a gram of potassium was converted into potassium amide in the course of fifteen minutes.

From the concept of these metal solutions as developed by Kraus[6] it would seem that the real reaction that occurs when the metal amide is formed is one between ammonia and the free or solvated electrons. The present investigation was undertaken for the purpose of obtaining data that would be of value in interpreting the nature of the reaction, and to show how the reaction rate varies with different metals and with different catalysts.

Experimental Method

The apparatus employed was designed to provide anhydrous and oxygen free reaction conditions at a constant temperature and a uniform rate of stirring, and to permit the collection of the hydrogen formed. Usually the catalyst in the form of a foil was used, and this foil itself served as a stirrer. In some work with powdered catalysts, an efficient glass stirrer was employed. The apparatus is shown in Fig. 1.

A reaction tube (A), Fig. 1, made of 30-mm. tubing and approximately 40 cm. long, fitted through a large rubber stopper into a Dewar tube (C), used to hold commercial liquid ammonia for a cooling bath. This Dewar tube was also provided with a small tube (D) through which dry air could be bubbled, a tube (E) through which air and ammonia vapor escaped, and a thermometer for noting the temperature of the bath. Through the side-arm (B) of the reaction tube passed a tube (F) connected with the supply tank of anhydrous ammonia dried over sodium. The top of the reaction tube was closed with a stopper through which passed the shaft of a stirrer, operated through a mercury seal (G) by means of a one-eighth horse-power motor (H); and tube (I), which, for the preliminary work, was connected to a mercury gage (J), used to regulate the pressure within the system.

In preparing for a run, the reaction tube was cleaned and dried, and then placed in position in the Dewar tube. The catalyst, in the form of a foil previously cleaned and prepared, as described in a later section, was fastened with wires of the same material to the glass rod forming the end of the stirrer shaft, and this placed in position. Other connections, as shown in Fig. 1, then were completed. By a combination of cooling and pressure, condensation of ammonia vapor was carried out until 50 cc., the volume

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[1] This paper is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Harry L. Kahler, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy (1934).

[2] Joannis, *Compt. rend.*, **109**, 900 (1889).

[3] Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900).

[4] Franklin and Stafford, *ibid.*, **28**, 83 (1902).

[5] Franklin, THIS JOURNAL, **27**, 820 (1905).

[6] Kraus, *ibid.*, **30**, 1323 (1908).

arbitrarily chosen for all reactions, was present, as shown by a calibrated mark on the tube. Then the outlet tube (I) was disconnected from the gage (J) and connected with a gas collection system. This consisted of a safety bottle containing a little mercury, an adsorption bottle containing mercury and dilute hydrochloric acid, and a gas buret. The purpose of the safety bottle was to ensure that no water vapor diffused back into the system, a procedure which did occur in runs of long duration when but one bottle was used. When a number of small samples, each for a definite interval of time, were to be collected for the same run, the single gas buret was replaced by a group of 90-cc. test-tubes fastened on the outer edge of a wooden circular disk.

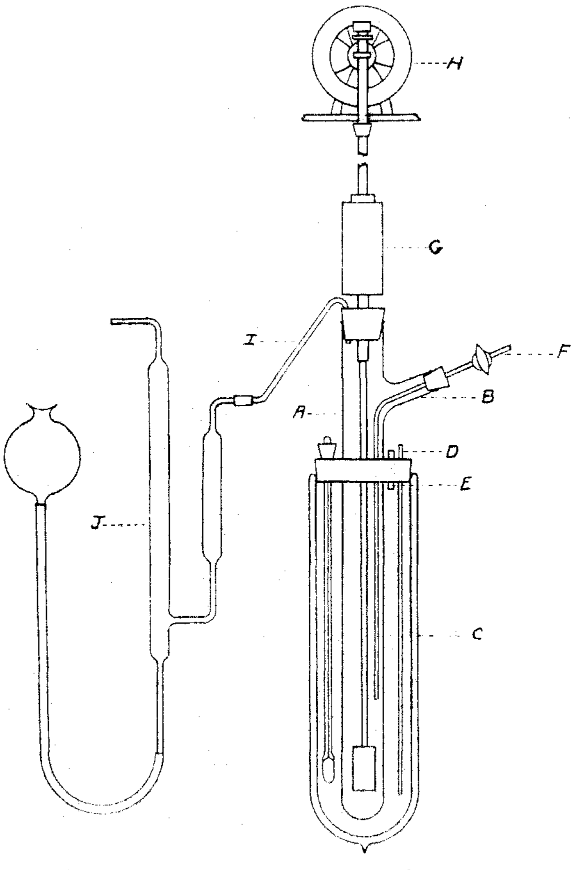

Fig. 1.—Apparatus for measurements in heterogeneous catalysis.

With the apparatus assembled for the run, the stirrer was tested and set at the desired speed. For reasons shown later, a speed of 250 r.p.m. was adopted and maintained within ± 5 r.p.m. for all runs. The temperature of the system was adjusted at $-33.5°$ for a reaction in which a vigorous evolution of hydrogen occurred and at $-34°$ for a slow reaction with slight evolution of hydrogen. Experience showed that, at these temperatures, the rate of condensation closely approximated the rate of evaporation of ammonia so that the volume of 50 cc. remained constant throughout the reaction.

The alkali metal was prepared by cutting and trimming to the size desired under petroleum ether, quickly transferring to a small weighing bottle filled with dry nitrogen, evaporating the petroleum ether by a stream of dry nitrogen and weighing. Then, using long tweezers, the alkali metal was dropped through the side-arm of the reaction tube, from which a current of ammonia was issuing to prevent entrance of air or moisture. The side-arm was closed immediately, the stirrer turned on, and a stop watch snapped. Throughout the run, temperature and stirring were maintained constant. The end of the run was judged by the disappearance of the blue color of the metal. This color end-point can be estimated accurately and shows an extremely low concentration of metal, since the color is distinct at a concentration of 0.000025 *N*. After this, the reaction tube was swept out with ammonia gas to remove all traces of hydrogen. The gas collected was analyzed for hydrogen by the Hempel explosion method. Test experiments showed that the loss of hydrogen seldom exceeded 1 cc.

In a number of experiments, after the first sample of metal had reacted completely, and the hydrogen had been swept from the apparatus, a second sample of metal was dropped and the time of reaction and amount of gas formed again determined. Similarly, other samples were added. Such runs, where the same set-up was used for a series of observations, will be referred to as consecutive runs.

In many of the earlier runs, a small amount of white insoluble material remained after the reaction was complete. The presence of this precipitate was found to be due to traces of moisture or air in the reaction system. The safety bottle of the gas collection system was necessary to eliminate all water vapor, and thorough sweeping out of the system with ammonia and rapid handling of the metal were necessary to ensure no oxide formation. All experiments in which there was any evidence of an insoluble residue were discarded.

Effect of Stirring.—Since the reaction between an alkali metal and liquid ammonia in the absence of a catalyst is very slow, the reaction that does occur in this work can be assumed to take place wholly on the surface of the catalyst. Therefore, the rate of supplying the reactants to this surface is a dominating factor in the time of reaction and this rate of supply is largely dependent on the mechanical stirring, although some stirring always occurred due to the liberation of hydrogen in the reaction. To determine how the rate of stirring effected the time of reaction, several consecutive runs were carried out in which the same weight of alkali metal was used, but the rate of stirring varied widely. The results for such a run using platinized platinum and for a run using rusted iron as catalyst are plotted in Fig. 2. The two curves are not identical, since different catalysts and different weights of metal were used, but they are of the same form. The time for reaction increased markedly with decrease in the rate of stirring, for stirring rates below 200 r.p.m. But above 250 r.p.m. there is but little change in the time of reaction. The rate of 250 r.p.m. was adopted for all experiments.

Effect of Potassium Amide on the Reaction Time.—In the above experiments, where successive samples of potassium reacted, the question naturally arises as to whether the presence in solution of the reaction product, potassium amide, influences the time of reaction. That it does not, is shown in Table I. Here are given the results of several experiments in which nearly equal weights of potassium were added, first, with little or no potassium amide being present, then with an appreciable amount of the amide already in the solution.

TABLE I

EFFECT OF POTASSIUM AMIDE ON REACTION TIME

Expt.	Catalyst	K, g.	KNH_2, g.	Time, min.
335b	Platinized	0.0354	0.0760	5.7
335g	platinum	.0364	.9330	5.8
187	Platinized	.0523	.0000	6.9
187f	platinum	.0521	2.9346	7.1
568c	Rusted	.0057	0.1287	3.0
568h	iron	.0057	.9745	2.9

Preparation of the Catalyst.—In the early experiments, considerable difficulty was experienced in securing check results. With the same catalyst on different days, different times of reaction were obtained. It was discovered that all the different catalysts, except rusted iron, would give consistent results if they were kept for a short time under reduced pressure and then exposed to ammonia gas. Consequently, a catalyst just prior to use, was put in a 30-mm. tube which was then sealed to an evacuation system, and evacuated for a period of not less than one-half hour at a pressure of 0.02 mm. Before the tube was opened to remove the catalyst, it was filled with ammonia gas. Because the platinized platinum required more delicate handling, so that the electrolytic deposit would not be injured, it was placed in a desiccator which was evacuated to about 1 mm. With this preliminary treatment, reproducible results were obtained with all but rusted iron.

With rusted iron, obtained by moistening pure iron foil and allowing it to stand in air for several hours, a different behavior was observed. This catalyst was not constant after evacuation, but became more efficient and finally gave constant results as successive samples of potassium were added. Experimental evidence for the constancy of four different catalysts is given in Table II where the times of reaction for nearly equal weights of potassium agree.

TABLE II

CONSTANCY OF CATALYST

Expt.	Catalyst	K, g.	Time, min.
628	Platinized	0.1141	9.5
628a	platinum	.1164	9.3
628b		.1151	9.1
538	Nickel	.0054	22.2
538a		.0059	21.1
558		.0058	21.0
558a		.0058	20.9
506a	Smooth	.0057	65.0
506b	platinum	.0059	65.0
511		.0061	69.0
511a		.0057	66.0
568a	Rusted	.0307	5.5
568f	iron	.0304	5.8
644b		.2332	12.6
644c		.2300	12.2

That consistent and more efficient catalysts were obtained by evacuation and then exposure to ammonia gas, supports the view that without this treatment there is an adsorbed air film on the catalyst which definitely reduces its effectiveness. This view is also strengthened by the following observations made with nickel foil. When the foil, after evacuation, was first exposed to pure oxygen in place of ammonia, the catalyst was less efficient and check results could not be obtained. Similarly, exposure to pure nitrogen after evacuation gave a poorer and inconsistent catalyst.

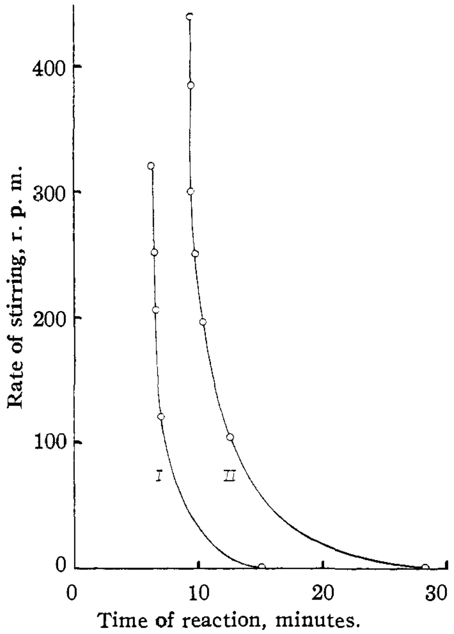

Fig. 2.—Effect of stirring rate on the time of reaction for the conversion of potassium to potassium amide; Curve I, using rusted iron as catalyst and 0.065 g. of potassium; Curve II, using platinized platinum as catalyst and 0.020 g. of potassium.

The explanation for the behavior of rusted iron may be deduced from the change in appearance of the catalyst as the first reaction proceeded. At the start the rust deposit was red in color. With the addition of potassium, this became black. It is believed that there was a reduction of a ferric compound to a ferrous compound, brought about by the potassium first added. That black ferrous oxide is a better catalyst than red ferric oxide was definitely shown by work done with powdered catalysts and reported in a later section.

Comparison of Catalysts.—The efficiency as catalysts of eleven different foils, each a rectangular strip 5.50 by 2.55 cm., with thickness varying from 0.01 to 0.15 cm., and having an area of approximately 28 sq. cm. was determined. This area is only comparable for the smooth catalysts because with platinized platinum and rusted iron, the deposit increased the surface area many times. While no work was done in which the size of the foil was varied, in experiments using powdered catalysts it was determined that the rate of the reaction increased in direct proportion to the increase in the weight of the powdered catalyst present.

The following foils were used: platinum, silver, zinc, copper, and nickel were all smooth foils of high purity; the iron foil was a sample obtained from the American Rolling Mill Company, 99.8% iron; tantalum and columbium, each 99.9% pure, were obtained from the Department of Metallurgy of the University of Cincinnati. All of these foils were highly polished before use with fine carborundum powder. The platinized platinum was prepared by depositing platinum from a 3% platinic chloride solution until a black uniform coat was obtained, and this subjected to electrolysis in dilute sulfuric acid to remove adsorbed impurities. The gray platinum was prepared by subjecting platinized platinum to a dull red heat for a few minutes. Rusted iron foil was prepared by wetting pure iron and allowing it to remain in contact with moist air until the surface was covered with small patches, these small patches being more stable under the condition of stirring than a heavier deposit. After preparation and between runs, foils were kept in a desiccator over phosphorus pentoxide. The relative value of the catalysts is shown in Table III.

TABLE III

RELATIVE EFFICIENCY OF CATALYSTS

Catalyst	K, g.	Time, min.
Platinized platinum	0.0057	2.6
Rusted iron	.0057	3.1
	.0057	3.1
Nickel	.0058	21
	.0059	21
Pure iron	.0050	44
	.0051	44
Smooth platinum	.0057	66
	.0057	65
Zinc	.0058	86
	.0059	71
Copper[a]	.0061	109
	.0057	162
	.0059	239
Silver	.0054	252
	.0059	245
Gray platinum	.0058	556
Tantalum	.0056	Over 1000
Columbium	.0058	Over 1000
No catalyst	.0051	Over 1500

[a] It was not possible to obtain check results with copper foil. This work was complicated by the presence of small black particles in the solution after the reaction had finished. The reaction will need further investigation.

Powdered Catalysts.—The experiments with powdered catalysts were carried out before the experimental procedure was standardized satisfactorily, so that the observations are more of a qualitative nature, but do serve to establish the relative value of five powders. Using sodium, the results were not consistent, as was also observed using foils, but did indicate the relative efficiency of the powdered catalysts to be as follows: (1) ferrous oxide; (2) ferric oxide; (3) magnetic iron oxide; (4) iron; (5) aluminum. The first four were all good catalysts, while the aluminum powder had practically no catalytic activity. With potassium, satisfactory results were obtained, and these confirmed the above rating with the ferrous oxide definitely superior to the others. Using powdered ferrous oxide, it was also shown that the time of reaction was inversely proportional to the weight of catalyst present.

That it was not possible to obtain consistent results for the reaction between sodium and ammonia with the catalyst either as a foil or powder, is believed due to the presence of sodium amide formed in the reaction. In one experiment, a sample of sodium weighing 0.1 g. required fourteen minutes to react, using a platinized platinum catalyst. A successive sample of the same weight required one hundred and thirty-five minutes, while a second successive sample did not finish in six hours. The poisoning effect might be due to the slight solubility of sodium amide, which is reported to be soluble in liquid ammonia to the extent of one gram per liter.[7] More likely it is adsorption of the sodium amide by the catalyst rather than simple precipitation that is involved. Thus, in several runs with amounts of sodium so small that the sodium amide formed was far less than the amount needed to saturate the solution, the catalyst was less efficient for the reaction with either sodium or potassium In a later paper, it will be shown that if an appreciable amount of potassium amide is already in solution, the poisoning effect of sodium amide is not observed. Under such conditions, the rate of the reaction of both sodium and potassium with ammonia is nearly identical.

Summary

An apparatus for studying the reaction between an alkali metal and ammonia, using catalysts in the form of foils and powder, is described. Platinized platinum, rusted iron, and nickel were the most efficient of the foils, while ferrous oxide was the best powdered catalyst. Sodium amide in solution poisons the catalyst, while potassium amide does not change its effectiveness.

CINCINNATI, OHIO RECEIVED SEPTEMBER 27, 1937

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(7) Bergstrom and Fernelius, *Chem. Rev.*, **12**, 43 (1933).