[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS. II. THE REACTION BETWEEN AMIDES OF THE ALKALI AND ALKALINE EARTH METALS AND ELEMENTS MORE ELECTROPOSITIVE THAN TIN

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Introduction

In the first paper of this series,[2a] it was shown that amalgamated aluminum initially reacts with sodium amide in the following manner: (1) $Al + 3NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3Na$. Subsequent reactions of sodium upon the solvent and of sodium amide upon the amphoteric base $Al(NH_2)_3$, lead to the formation of sodium ammono-aluminate, $Al(NH_2)_2NHNa.NH_3$. Magnesium and manganese later were found to react in a similar manner with potassium amide.[2b] The present investigation was undertaken in order to show the extent to which reactions of this type occur.

Discussion

Potassium amide has previously been found to react with aluminum, magnesium, zinc, calcium, sodium and lithium with the formation of ammono salts.[3] In the present work, cerium, lanthanum and gallium were found to react slowly with solutions of potassium amide, while cadmium, chromium, iron, cobalt, molybdenum, tungsten and thallium either failed to react or reacted only to a slight extent. In general, the more electropositive a metal is, the more readily does reaction occur with potassium amide.

The initial reaction in all of the cases examined was found to be of the type of Equation 1. The less electropositive metal, for instance manganese, reacted with potassium amide to form an amide, $Mn(NH_2)_2$, of very low solubility in liquid ammonia. This amide in turn reacted with potassium amide to form an ammono salt, in this case potassium ammonomanganite, $Mn(NHK)_2.2NH_3$.[4,5]

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[2] (a) THIS JOURNAL, **45**, 2788 (1923); (b) **46**, 1548, 1552 (1924).

[3] (a) Franklin, THIS JOURNAL, **35**, 1463 (1913); (b) **37**, 2300 (1915). (c) Fitzgerald, *ibid.*, **29**, 660 (1907). (d) Franklin, *J. Phys. Chem.*, **23**, 41 (1919); (e) **23**, 50 (1919).

[4] The initial reaction may be represented, in general terms, by the equation, $M^n + nANH_2 \rightleftharpoons nA + M(NH_2)_n$, where M is a metal of positive valence n, and A represents sodium or potassium. Subsequently, A reacts with the solvent, in the presence of M, which may act as a catalyst, and ANH_2 reacts with the amphoteric base, $M(NH_2)_n$, to form an ammono salt. Kraus, Ref. 5 a, p. 184.

[5] Reduction reactions of this nature have been discussed by (a) Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 175 (1924), and (b) Kraus and Kurtz, THIS JOURNAL, **47**, 43 (1925).

The reactions between potassium amide and manganese, zinc, lanthanum, cerium and gallium were in general too slow to lead to the formation of characteristically blue solutions of potassium. The catalytic effect of the less electropositive metal was sufficiently great to cause the potassium to react with the solvent as rapidly as liberated from the potassium amide by reduction in accordance with Equation 1. A faint blue color was observed in one reaction between potassium amide and amalgamated zinc, and a similar result was obtained with one specimen each of manganese and lanthanum.

That the equilibrium represented by Equation 1 occurs in all reactions between the more electropositive metals and potassium amide is most readily shown by carrying out the reaction in the presence of mercury, which absorbs the potassium as rapidly as it is formed. Potassium amide was found to react with the amalgams of magnesium, aluminum, zinc and cadmium in such a manner that for each atom of the metal entering the reaction, n atoms of potassium were liberated and dissolved by the mercury. The letter n represents the principal positive valence of the less electropositive metal. (See Table II.) It was determined qualitatively that lanthanum and cerium react with potassium amide in a similar manner. G. McP. Smith has shown that equilibria of this same type exist in water.[6] Thus, potassium hydroxide reacts with dilute amalgams of magnesium, strontium, barium and calcium to form some potassium amalgam and a corresponding amount of the hydroxide of the less electropositive metal. The reaction between solutions of strong aquo bases and zinc or aluminum may best be explained by the assumption of similar equilibria: thus, initially, $Al + 3KOH \rightleftharpoons Al(OH)_3 + 3K$.[7] The very rapid reaction of potassium with the solvent and the reaction of potassium hydroxide with the amphoteric base aluminum hydroxide leads to the formation of potassium aquo-aluminate.[8] Such a mechanism is very probable in view of the many analogies already known to exist between reactions in water and in ammonia.[9]

It was found, in the present work, that if the electrodes of a cell $Al \mid NaOH, Ca(OH)_2$ [or $Ba(OH)_2$] aq. $\mid Hg$ be short-circuited for some time, the mercury reacts slowly with dil. hydrochloric acid, indicating the

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[6] Smith, *Am. Chem. J.*, **37**, 506 (1907), and subsequent articles in THIS JOURNAL and *J. Phys. Chem.*

[7] Ref. 5 a, p. 184. Ref. 5 b, p. 45. Ref. 2 a, p. 2790. Compare Heyrovsky, *Proc. Roy. Soc.*, **102A**, 628, 637 (1923).

[8] It should be remembered that aluminum reacts readily with water alone, provided its surface has been "activated" by amalgamation or by the action of aqueous solutions of bases. For this reason it is probable that the reaction between dilute solutions of bases and aluminum is due both to the action of the solvent and to the action of the base on this metal.

[9] Franklin, THIS JOURNAL, **46**, 2139 (1924).

presence of small amounts of sodium and calcium (or barium). Similar but less definite results were obtained in the case of cells containing an aluminum or a zinc rod immersed in a solution of sodium hydroxide. These experiments indicate that the hydrogen results from the action of the alkali metal on water following its reduction from the base according to Equation 1 rather than by direct displacement from water by the original metal. Otherwise, one should expect only hydrogen to be liberated at the mercury surface.

Experimental Work

Manipulation.—The reactions described in this paper were all carried out in liquid ammonia reaction tubes at room temperatures according to the methods of Franklin.[10]

Potassium Ammonocerite and Ammonolanthanite, $Ce(NHK)_3.2\text{–}3NH_3$, $La(NHK)_3.2\text{–}3NH_3$.—Ammono salts of approximately the composition given above may be obtained by the action of an excess of potassium amide upon the corresponding metal or, more readily, upon a salt of the metal, such as the bromide or iodide. Potassium ammonocerite and lanthanite are apparently amorphous, light greenish-yellow in color and are very slightly soluble in liquid ammonia. These salts, in common with all other ammono salts, react very vigorously with water.

The specimens were washed thoroughly with liquid ammonia, dried in a vacuum at room temperature, slowly hydrolyzed by means of water vapor, and then dissolved in dil. hydrochloric acid preparatory to analysis. Cerium and lanthanum were precipitated as oxalate and determined as oxide. Potassium was weighed as the sulfate or chloride. Nitrogen was

TABLE I

ANALYTICAL DATA

Salt	Wt. of subst. dried in a vacuum at (T)° G.	Wt. of CeO_2 or La_2O_3 in () of subst.	Wt. of K_2SO_4 in () of subst.	Wt. of N in () of subst.
	(−40°) 0.8840			
Cerite 1[a]	(20°) 0.8819	$(^2/_5)$ 0.1847	$(^2/_5)$ 0.2547	$(^1/_5)$ 0.03826
Cerite 2[c]	(20°) .3115	$(^1/_4)$ .0405	$(^1/_4)$ .0553	$(^1/_4)$ .01742
Cerite 3[b]	(20°) .3977	$(^1/_2)$ .1018	$(^1/_2)$ .1159KCl	$(^1/_4)$ .02248
Lanthanite 1[a]	(20°) .2615	$(^1/_4)$ .0333	$(^1/_4)$ .0496	$(^1/_4)$ .01507
Lanthanite 2[b]	(20°) .3106	$(^1/_2)$ .0812	$(^1/_2)$ .1141	$(^1/_4)$ .01728
Lanthanite 3[c]	(20°) .2892			
	(140°) .2714	$(^1/_2)$ .0706	$(^1/_2)$ .1027	$(^1/_2)$ .02657

[a] Prepared from potassium amide and the metal.

[b] Prepared from cerium or lanthanum iodide and an excess of potassium amide.

[c] Prepared as above, but from cerium bromide.

For the method of preparation of these salts, see Bergstrom, *J. Phys. Chem.*, **29,** 162 (1925).

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[10] Franklin, THIS JOURNAL, **27,** 832 (1905); **29,** 1694 (1907); Ref. 3a, p. 1460; *J. Phys. Chem.*, **15,** 915 (1911); **16,** 694 (1912).

TABLE II

ANALYSES OF POTASSIUM AMMONOCERITE AND LANTHANITE

Dried in a vacuum at room temperatures

Calcd. for $Ce(NHK)_3.2.5NH_3$		Found 1	Found 2	Found 3	Calcd. for $La(NHK)_3.2.5NH_3$		Found 1	Found 2	Found 3
Ce	40.6	42.6	42.3	41.7	L	40.4	43.4	44.6	41.6
N	22.3	21.7	22.4	22.6	N	22.4	23.0	22.2	23.4
K	34.0	32.4	31.9	30.6	K	34.1	34.0	33.7	31.9

determined as ammonia by distillation of a portion of the original acid solution of the specimen with sodium hydroxide in the customary manner.

Lanthanite specimen No. 3, dried in a vacuum at 140°, corresponds in composition approximately to $La(NHK)_3.1.5NH_3$. The metal used in the preparation of the lanthanite specimens 1 and 2 contained in small amounts other rare earth metals of higher atomic weight, which appear in the analysis as lanthanum. Both of these preparations, as well as cerite Preparation 1 contained small amounts of unattacked metal.

Potassium Ammonogallate.—Potassium amide reacts slowly with gallium to form an extremely soluble potassium ammonogallate which, however, was not obtained free from an excess of potassium amide. Potassium in ammonia solution was found to react slowly with gallium at room temperatures with the formation of potassium amide and a gray-black potassium-gallium alloy of high gallium content. Due to the potassium liberated in the initial reaction, which is analogous to the reaction expressed by Equation 3, an alloy of this nature is formed by the action of potassium amide on gallium.

Action of Basic Amides on Other Elements.—The action of the amides of potassium, sodium, lithium and calcium on certain other elements has been summarized in Table III. (In liquid ammonia, room temperatures.)

TABLE III

THE ACTION OF LIQUID AMMONIA SOLUTIONS OF BASIC AMIDES UPON METALS

Base	Metal	Form of metal	Concn. of base N	Time of action Months	Action
KNH_2	Cd	Rod	1.7 N	7	X[b]
KNH_2	Cr	Lump	0.5 N	4	X
KNH_2	Tl[a]	Lump	Moderately strong	8	v. s.
KNH_2	Mo	Lump	Moderately strong	12	e. s.
KNH_2	W	Lump	Moderately strong	12	v. s.
KNH_2	Fe	Wire	Moderately strong	6	X
KNH_2	Co	Sheet	Moderately strong	6	X
$NaNH_2$	Mn	Lump	Saturated, excess of solid	4	s.
$NaNH_2$	Ga	Liquid	Saturated, excess of solid	3.5	s.
$NaNH_2$	Ce	Lump	Saturated, excess of solid	7	s.
$LiNH_2$	Al amalg.		Saturated, excess of solid	4.5	s.
$Ca(NH_2)_2$	Al amalg.		Saturated, excess of solid	4	X

[a] Impure.

[b] X, no detectable action in the period state; e. s., extremely slight action; v. s., very slight action; s., a little action.

TABLE IV

THE ACTION OF LIQUID AMMONIA SOLUTIONS OF POTASSIUM AND SODIUM AMIDES UPON CERTAIN AMALGAMS

Metal, M, initially in amalgam	Zn^a	Zn^c	Zn^d	Al^a	Al^a	Al^a	Mg^d	Mg^b	Mg^d	Cd^a
M found in prod. of reaction, detd. as	$Zn_2P_2O_7$	$Zn_2P_2O_7$	$Zn_2P_2O_7$	Al_2O_3	Al_2O_3	Al_2O_3	$Mg_2P_2O_7$	$Mg_2P_2O_7$	$Mg_2P_2O_7$	$CdSO_4$
	0.3896 g.	0.5114	0.2326	0.0998	0.0881	0.0561	0.2049	0.2062	0.1425	0.4143
Alkali metal, A, found in mercury, detd. as	KCl	K_2SO_4	KCl	KCl	KCl	NaCl	KCl	KCl	KCl	K_2SO_4
	0.3718 g.	0.5937	0.2258	0.4298	0.3898	0.1832	0.2711	0.2708	0.1959	0.3547
Ratio of atoms of alkali metal A, to the metal M	1.95	2.03	1.98	2.95	3.03	2.85^e	1.98	1.96	2.06	2.05

[a] Amalgam in excess.

[b] Amalgam in large excess.

[c] Potassium amide in excess.

[d] Potassium amide in large excess.

[e] At one stage of the reaction the solution was blue, resulting in less than the theoretical amount of sodium in the amalgam.

Action of Potassium and Sodium Amide on Amalgams.—A solution of potassium amide was found to react readily with liquid amalgams of magnesium, zinc and cadmium with the initial formation of bulky white precipitates, when first produced, approximating the corresponding amides in composition but containing potassium in quantity varying with the relative proportion of potassium amide and amalgam used. Amalgamated aluminum in contact with an excess of mercury was attacked less readily than the above-mentioned amalgams by a solution of sodium or potassium amide without the formation of appreciable quantities of aluminum amide. A dilute iron amalgam was very slowly attacked by a solution of potassium amide.

Potassium or sodium amide, formed in one leg of a two-legged reaction tube,[10] was transferred to the other leg, which contained the desired amalgam. The product of the reaction, if a solid, was transferred as completely as possible in suspension to the second leg of the reaction tube—a rather tedious process; if soluble in ammonia it was transferred simply by washing the amalgam. The mercury was treated with water and dil. hydrochloric or sulfuric acid, the less electropositive metal separated by common analytical methods, and the alkali metal weighed as sulfate or chloride. Zinc, cadmium, aluminum and magnesium were determined by the customary methods in the acid solutions of the material separated from the amalgam. The results of these experiments are given in Table IV.

In conclusion, the author wishes to thank Dr. Charles A. Kraus for his kind and helpful interest in this work.

Summary

1. A study has been made of the reactions between potassium and sodium amide in liquid ammonia and elements more electropositive than tin or lead. The initial reaction, where reaction occurs, involves a partial replacement of the more electropositive metal by the less electropositive one, as typified in the equation, $Al + 3KNH_2 \rightleftharpoons Al(NH_2)_3 + 3K$. Secondary reactions cause the displacement of equilibria of this type and result in the formation of ammono salts. It was found that, in general, the more electropositive an element is, the more readily does it react with a solution of potassium amide.

2. Potassium ammonolanthanite, $La(NHK)_3.2\text{–}3NH_3$, and potassium ammonocerite, $Ce(NHK)_3.2\text{–}3NH_3$, have been prepared in an impure condition.

3. The suggestion is made that the mechanism of the reactions between solutions of bases of the water system and aluminum or zinc is analogous to that discussed in Paragraph 1 above.

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