[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Catalytic Formation of Potassium Nitrite from Potassium Nitrate in Liquid Ammonia

BY F. W. BERGSTROM

Introduction and Discussion of Results

A solution of potassium amide in liquid ammonia reacts with quinoline to form a resinous or tarry mixture, from which no definite compounds can be isolated, other than occasional traces of 2-aminoquinoline.[1] In the presence of potassium nitrate, both 2- and 4-aminoquinolines are obtained as the potassium salts, in total yields approximating 65% of the theoretical as calculated from the equation[2]

$$C_9H_7N + 2KNH_2 + KNO_3 \longrightarrow C_9H_6N{\cdot}NHK + KNO_2 + NH_3 + KOH \quad (1)$$

Since the yield of nitrite, as determined by volumetric means, was frequently above 100% of the theoretical, it was apparent that a secondary reaction was occurring at the same time. In the present work, it was discovered that the disturbing factor was the ferric oxide used as a catalyst for the reaction between metallic potassium and liquid ammonia, in which hydrogen and potassium amide are formed. The latter, whether in excess or not, was found to convert a solution of potassium nitrate at room temperature into potassium nitrite, nitrogen, potassium hydroxide and ammonia, in accordance with the equation,

$$3KNH_2 + 3KNO_3 \longrightarrow 3KOH + 3KNO_2 + N_2 + NH_3 \quad (2)$$

Ferric oxide, cobaltic oxide, nickelous oxide and cupric oxide were all fairly active catalysts for this reaction. Mangano-manganic oxide (Mn_3O_4) was a somewhat less effective catalyst, while aluminum oxide, zinc oxide and chromium oxide (Cr_2O_3) were the poorest investigated. The reaction of equation (2) appears in some measure to be autocatalytic, since there is evidence to indicate that potassium hydroxide very slowly accelerates the formation of nitrite from nitrate.

In all cases, the catalyst is slowly attacked by the potassium amide to give potassium hydroxide[3] and a potassium ammonometallate of the type of potassium ammonocuprite, $CuNK_2{\cdot}xNH_3$. Several substances therefore contribute to the catalytic activity ascribed to the metallic oxides. Metallic iron, in the form of fine wire, has very little influence on the reaction of equation (2), though it is possible that the finely divided metal that one obtains superficially by treating ferric oxide with solutions of metals in liquid ammonia is catalytically active.

Equation (2) was verified by determination of nitrogen evolved in the reaction, by determination of nitrite formed, by finding the loss in weight ($N_2 + NH_3$) resulting from the reaction and by titrating the potassium hydroxide formed in those reactions where excess potassium nitrate was used.

The practical independence of the N_2/KNO_2 ratio with variations in time, and with variations in the KNH_2/KNO_3 ratio, excludes the otherwise plausible mechanisms expressed by equations (A) and (B), and summarized in equation (2).

$$2KNH_2 + 3KNO_3 \longrightarrow NH_3 + 4KNO_2 + KOH \quad (A)$$

$$KNH_2 + KNO_2 \longrightarrow N_2 + 2KOH \quad (B)$$

$$3KNH_2 + 3KNO_3 \longrightarrow NH_3 + 3KNO_2 + 3KOH + N_2 \quad (2)$$

This involves (A) an oxidation analogous to the known air oxidation of potassium amide[4] and (B) a reaction which has been demonstrated to be very slow.

Potassium amide slowly reacts with potassium nitrite in liquid ammonia in the presence of the oxides of cobalt and iron to form potassium hydroxide and nitrogen, in accordance with the equation

$$KNO_2 + KNH_2 \longrightarrow 2KOH + N_2 \quad (3)$$

The reaction is exceedingly slow in the absence of a catalyst. Sodium amide and sodium nitrite, however, react explosively when heated in the solid or fused states.[5] One may speculate and say that the first reaction product is a mixed aquo-ammono nitrite of the composition ON·NHK, which is unstable and decomposes into potassium hydroxide and nitrogen. Fernelius and Watt[6] obtained diphenylamine, nitrogen and potassium hydroxide instead of the expected ON·NHK by

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[1] Bergstrom, THIS JOURNAL, **56**, 1750 (1934).

[2] Bergstrom, *J. Org. Chem.*, **2**, 414 (1937).

[3] Potassium oxide may well be formed at first, but it will be reversibly ammonated in accordance with the equation $K_2O + NH_3 \leftrightarrows KNH_2 + KOH$. Potassium oxide is probably present in appreciable quantity only in strong potassium amide solutions: Bergstrom, THIS JOURNAL, **53**, 3038 (1931).

[4] Kraus and Whyte, *ibid.*, **48**, 1781 (1926).

[5] Browne and Wilcoxson, *ibid.*, **48**, 682–690 (1926); Bergstrom and Fernelius, *Chem. Rev.*, **12**, 57, 64 (1933).

[6] Fernelius and Watt, THIS JOURNAL, **55**, 3482–3485 (1933).

the action of potassium amide on diphenylnitrosoamine, $(C_6H_5)_2N{\cdot}NO$, indicating that the potassium aquo-ammononitrite is unstable.

Franklin and his students[7] found that yields of potassium azide as high as 75% of the theoretical were obtained by heating potassium nitrate with an excess of potassium amide in glass reaction tubes at temperatures between 100 and 130°, in accordance with the equation

$$KNO_3 + 3KNH_2 \longrightarrow 3KOH + KN_3 + NH_3 \quad (4)$$

Azide was not formed when the above reactants were heated in a steel tube, an observation that is reasonable in view of the present experiments, since the ferric oxide on the inner surface of the tube would cause the reaction to follow equation (2) and give potassium nitrite and nitrogen. The formation of azide in the manner of equation (4) has been qualitatively verified in the present work, by heating potassium nitrate with an excess of potassium amide in a straight glass tube, in accordance with the methods of the present article. It is improbable that azide is the first product of the action of potassium amide on potassium nitrate in liquid ammonia at room temperatures, since sodium azide is not decomposed to nitrogen in the presence of ferric oxide and a large excess of potassium amide.

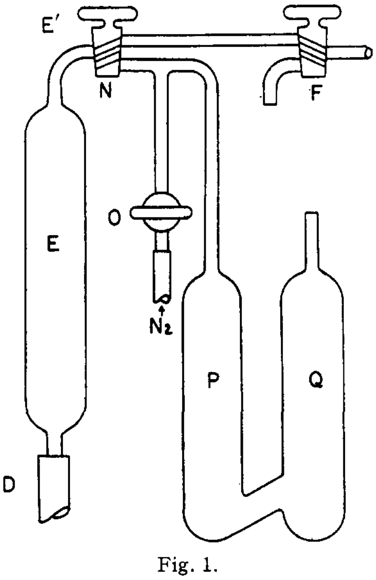

Fig. 1.

It was hoped that the replacement of potassium amide in the reaction of equation (2) by potassium anilide or potassium β-naphthylamide might lead to the formation of a tertiary aromatic amine instead of ammonia, in accordance with the equation

$$3C_6H_5NHK \text{ (or } 3C_{10}H_9NHK\text{-}\beta) + 3KNO_3 \longrightarrow 3KNO_2 + 3KOH + N_2 + (C_6H_5)_3N \text{ [or } (C_{10}H_9)_3N] \quad (5)$$

Since the desired products were not obtained, it is probable that the reaction will proceed only in the presence of a base of the approximate strength of potassium amide.

Experimental Part

Most of the reactions listed in Table I were carried out at room temperatures (18–25°) in straight glass tubes, partly in accordance with manipulations described in earlier articles.[8,9] The following differences may be recorded.

(1) After removal of the iron wire catalyst from the cooled reaction tube, the oxide listed in Table I, Column 4, together with the well-dried potassium nitrate, was introduced through a short stem funnel inserted in C′ of Fig. 2, ref. 8.

(2) In some experiments potassium amide was made from potassium with the use of an oxide catalyst; no additional catalyst was added with the potassium nitrate. There was no significant change in the rate of formation of nitrite.

(3) Gases formed in the reaction were analyzed for hydrogen (slow combustion pipet) and, in a few cases, for nitrous oxide (combustion with pure hydrogen in a slow combustion pipet).

(4) Since oxygen of the atmosphere reacts with potassium amide in the manner of the equation,[4] $4KNH_2 + 3O_2 \longrightarrow 2KOH + 2KNO_2 + 2NH_3$, it was necessary to fill the partially evacuated reaction tube with nitrogen, after collection of gases and prior to evaporation of the solvent ammonia. The apparatus of Fig. 2, reference 8, was modified by interposing the mercury bubbler, PQ, between E′ and F (see Fig. 1 of this article; the lettering of the common features on the two diagrams is the same). P and Q are about a third filled with dry mercury.

Dry nitrogen was introduced under slight pressure through O and allowed to bubble through Q to displace air within the apparatus. Stopcock N was carefully turned so that the system D, E, E′ was gradually connected with P, thus filling the reaction tube with nitrogen slightly above atmospheric pressure. After removal from the rubber adapter, C (Fig. 2 of ref. 8), the top of the tube was drawn out to a fine capillary and the whole allowed to warm up, whereupon solvent ammonia slowly evaporated. The capillary was cut off and a stopcock fastened on (with rubber tubing), after which the reaction tube was evacuated, and then clamped in an almost horizontal position with the precipitate higher than the stopcock. By slowly opening the stopcock under a water seal, a few cc. of water was drawn into the tube and the precipitate allowed to hydrolyze overnight under the influence of the water vapor.

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[7] Franklin, "The Nitrogen System of Compounds," A. C. S. Monograph No. 68, pages 142–143, The Reinhold Publishing Co., New York, N. Y., 1935; J. B. Harker, Thesis, Stanford University, 1927; F. Y. Chuck, Dissertation, Stanford University, 1925; Franklin, This Journal, **56**, 568 (1934).

[8] Bergstrom, *ibid.*, **56**, 1748 (1934).

[9] Bergstrom, *J. Org. Chem.*, **2**, 423 (1937).

TABLE I

THE ACTION OF POTASSIUM AMIDE ON POTASSIUM NITRATE AND POTASSIUM NITRITE IN THE PRESENCE OF CATALYSTS

No.	Millimoles KNH_2	Millimoles KNO_3	Catalyst, g.	NH_3[p]	Time of reaction, days	N_2, millimoles	%	KNO_2,[a] millimoles	%	Notes
1	15.4	10.0	Fe, 0.800	28	7	0.175	5.2	0.050	5.0	*b*
2	15.4	10.06	Fe_2O_3, 0.05	22	8	2.705	80.7	0.796	79.1	*c*
3	30.2	10.0	Fe_2O_3, 0.05	24.5	17	3.38	101	0.955	95.5	*d*
4	11.52	31.1	Fe_2O_3, 0.505	29.5	710	3.70	96.3	1.095	95.0	*e*
5	11.66	24.9	Fe_2O_3, 0.046	34	93	2.81	72.4	0.845	72.5	
6	10.54	31.8	Fe_2O_3, 0.445		117	3.38	96.4			
7	None	10.62	Fe_2O_3, 0.05	22	30	0.00	0.0	0.00	0.0	
8	26.4	8.9	None	32	142	0.960	32.0	present		*f*
9	28.2	6.97	None	26.5	0.38	0.232	10.0	0.035	5.0	*g*
10	15.4	10.0	None	18	7			0.020		
11	29.9	10.00	Co_2O_3, 0.137	26.5	9	3.32	99.6	0.976	97.6	*h*
12	32.5	10.37	Mn_3O_4, 0.214		59	3.67	106	1.00	96.4	*i*
13	31.7	10.14	NiO, 0.108		5	3.32	98.4	0.998	98.3	*j*
14	32.0	10.03	NiO, 0.201	29.5	61	3.36	100.5			
15	30.2	10.04	CuO, 0.120	35	18	2.71	81.0	.733	73.0	*k*
16	30.7	9.98	Al_2O_3, 0.121	31	80	2.96	89.0	.923	92.5	
17	31.2	10.02	Cr_2O_3, 0.106	24	596	1.77	53.0			
18	30.2	10.00	ZnO, 0.106	32	28	1.70	51.0	.486	48.6	
19	35.5	10.00	KOH, 0.280	27	7	0.453	13.6	.131	13.1	*l*
		KNO_2[m]						Consumed[n]		
20	16.6	9.40	Fe_2O_3, 0.05	22	9	0.16		0.09		
21	31.8	10.19	Co_2O_3, 0.114		547	3.39		3.35		
22	31.7	9.93	None	23.5	47	0.09		0.00		
23	20.7	NaN_3, 3.1	Fe_2O_3, 0.10	25.5	76	0.03				*o*

[a] In 0.1 aliquot portion. [b] 252 cm. of clean iron wire. The potassium was cut from a calibrated tube. Sodium nitrite was determined by the sodium azide method (ref. 11). [c] Gases were entirely nitrogen. Nitrous oxide was absent, since there was no significant contraction on burning with hydrogen (slow combustion pipet). [d] In a repetition of this (14-day reaction), 104% nitrogen and 84.1% potassium nitrite were obtained. In spite of a shorter time of reaction, more decomposition in the sense of equation (3) has occurred. [e] Potassium was contained in a weighed capsule, prepared according to the method of Kraus and Chiu, THIS JOURNAL, **44**, 2001 (1922). The iron wire catalyst was left in during the reaction. Potassium hydroxide, in $^1/_5$ aliquot, titrated after boiling out the ammonia, was 2.26 millimoles, or 98.2% of the theoretical. Nitrous oxide was absent. [f] Potassium from a calibrated tube. Iron wire catalyst removed before the introduction of the KNO_3. No visible KOH present. [g] Heated at 100–130°. Nitrite was determined by the sodium azide method (ref. 11). The yield of azide, determined by the method of Dennis and Browne, THIS JOURNAL, **26**, 597 (1904), was 43% of the theoretical. Since the solution was acidified before the precipitation of the silver azide, a certain amount of the latter was decomposed by reaction with nitrous acid (ref. 11). [h] No hydrogen present. In a repetition, 101% nitrogen and 96.1% nitrite were formed (12-day reaction), indicating a slight decomposition in accordance with equation (3). [i] Mn_3O_4 was prepared by igniting C. P. $MnCO_3$. Mn_3O_4 is a very poor catalyst for the $K \longrightarrow KNH_2$ reaction. A small amount of hydrogen (0.11 millimole) was formed, doubtless from the action of KNH_2 on metallic manganese, produced by the reduction of the oxide by potassium solution. [j] In a repetition (see expt. 14), 100.5% of the theoretical amount of nitrogen was obtained, indicating that NiO is not as active a catalyst for the decomposition of nitrite as Fe_2O_3 or Co_2O_3. [k] Potassium amide reacts with cupric oxide, as is shown by the following experiment. Finely powdered and ignited cupric oxide (0.481 g.) was added, at −33°, to the potassium amide from 1.02 g. of potassium (26.1 milliatoms) in a straight tube, in accordance with the manipulations described in this article. The iron wire used as a catalyst for the formation of the potassium amide was withdrawn before the reaction. After warming to room temperatures, a moderately rapid reaction took place, with the formation of a white precipitate and the evolution of gas. No apparent change occurred after the first few days, but the tube nevertheless was allowed to stand for five weeks, at the end of which time it was opened and found to contain 22.75 cc. nitrogen (standard conditions) or 1.005 millimoles (theory, 1.007 millimoles). The ammonia-soluble matter on hydrolysis gave a precipitate of cuprous oxide, indicating the presence of potassium ammonocuprite [Franklin, THIS JOURNAL, **34**, 1501 (1912)]. The reaction probably follows the equation, $6CuO + 18KNH_2 \longrightarrow 6CuNK_2 + N_2 + 10NH_3 + 6KOH$, disregarding ammonia of crystallization associated with the potassium ammonocuprite. Therefore, in expt. 15, nitrogen was formed by the action of potassium amide on the cupric oxide catalyst. If the total yield of nitrogen (2.71 millimoles) is decreased by the nitrogen from the catalyst ($^1/_6$ of 1.51 millimoles of CuO) one gets 2.46 millimoles (73.5%) in good agreement with the nitrite formed (73.0%). [l] The potassium hydroxide was prepared by adding 0.09 g. of water to the potassium amide solution, while cooled to −33°. The iron wire catalyst had previously been withdrawn. [m] C. P. dry potassium nitrite of 93.6% actual nitrite content was used. The weights of KNO_2 given in the table equal the weight of material used multiplied by 0.936. [n] Weight of nitrite used less weight of nitrite present at the end of the reaction. [o] Azide is therefore probably not an

intermediate in the reactions of potassium amide with potassium nitrate or potassium nitrite. [p] Volume of ammonia calculated from the internal diameter of the tube and the height of the liquid therein.

To complete hydrolysis, the tube was slowly tilted toward the horizontal, so that a very little of the water came into contact with the precipitate. To avoid too violent a reaction, which would result in an explosion, the tube was at once clamped so that the excess water ran back to the stopcock end. After a few hours, during which time the precipitate was slowly attacked by the small amount of liquid in contact with it, the process was repeated until eventually all of the solid was decomposed. The aqueous solution, together with the suspension of the catalyst, was withdrawn into a 50-cc. volumetric flask[10] and the tube washed out a number of times with small amounts of water. Five-cc. aliquots were taken for analysis (the catalyst first having been allowed to settle). Most of the analyses were made by the modified Coade–Werner method already described,[9] since blank runs showed that no appreciable amount of azide was formed. A few determinations were carried out by the sodium azide method of Oliveri-Mandalà.[11] In all cases, the correction was made for dissolved gases in the aqueous solution by first expelling the collected gas through the stopcock of the Lunge nitrometer, closing the stopcock, and boiling the water by lowering the levelling buret, or by applying a vacuum to the surface of the mercury contained in it. The volume of liberated gas (measured with mercury surfaces level) was added to the main volume collected. The solutions in the nitrometer were of course degassed before use.

Loss in Weight During the Reaction.—In accordance with a previously described method,[12] 1.0208 g. of potassium nitrate (dry, c. p.) reacted for eight days with the potassium amide from 0.792 g. of potassium in the presence of 0.02 g. of ferric oxide. The reaction tube, weighed evacuated at room temperature before and after the reaction, lost 0.1518 g. (theoretical loss [$N_2 + NH_3$, equation (2)] 0.1516 g.). The yield of nitrite was 95.5%.

Identification of Potassium Hydroxide as a Product of the Reaction.—The crystalline white precipitate formed by treating potassium nitrate with ferric oxide and an excess of potassium amide is difficult to wash free of nitrite and to separate from the oxide catalyst. The analyses therefore only approximate to the formula KOH. Titration of the latter was however carried out in one case (Table I, Note *e*).

The Attempted Formation of Tertiary Aromatic Amines.—Under the approximate conditions of expts. 2–3, Table I, 10 millimoles of potassium anilide reacted for ninety-five days with 10 millimoles of potassium nitrate in liquid ammonia. No gas was formed in the reaction, and no diphenylamine or triphenylamine was isolated. Similar results were obtained in a reaction involving potassium β-naphthylamide (233 days). About 60% of the β-naphthylamine was recovered after hydrolysis of the reaction mixture.

Formation of Azide.—In a preliminary experiment (expt. 9, Table I), azide was found to be formed in quantity when excess potassium amide was heated with potassium nitrate in liquid ammonia at a temperature between 100 and 130°. There also resulted a small quantity of nitrite, even though all catalysts apparently had been excluded. Because nitrous acid and hydrazoic acid react in the manner of the equation[11] $HNO_2 + HN_3 \longrightarrow H_2O + N_2O + N_2$, it is evident that azide cannot be determined accurately in the presence of nitrite by the Dennis–Browne method (Table I, note *g*).

Summary

1. In the presence of certain oxide catalysts, potassium amide reacts slowly with potassium nitrate in liquid ammonia at room temperatures, in accordance with the equation

$$3KNH_2 + 3KNO_3 \longrightarrow 3KOH + N_2 + NH_3 + 3KNO_2$$

Ferric oxide, cobaltic oxide and nickelous oxide are particularly good catalysts, cupric oxide and manganese (Mn_3O_4) are fairly effective, while zinc oxide and aluminum oxide are very poor. Even potassium hydroxide appears to be a weak catalyst, so the reaction expressed by the above equation is in some measure autocatalytic. Azide is not formed (or it is formed only in traces) in catalyzed room temperature reactions, though it is obtained at higher temperatures when the catalyst is omitted.

2. Potassium nitrite reacts at an extremely slow rate with a liquid ammonia solution of potassium amide at room temperatures, and in the presence of ferric oxide or cobaltic oxide, to form nitrogen and potassium hydroxide, in accordance with the equation

$$KNO_2 + KNH_2 \longrightarrow 2KOH + N_2$$

STANFORD UNIVERSITY, CALIFORNIA

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[10] *Cf.* Fernelius and Bergstrom, *J. Phys. Chem.*, **35**, 750 (1931).

[11] Oliveri-Mandalà, *Gazz. chim. ital.*, **51**, I, 138–140 (1921).

[12] Bergstrom, THIS JOURNAL, **53**, 4068–4069 (1931).