sodium perchlorate for potassium chloride and again the rates obtained were identical, within experimental error. This also indicates specifically that the chloride ion concentration has no effect on the rate.

Figure 3 shows a plot of log k' against $p\mathrm{H_c}$. This plot is seen to be a straight line with a slope approaching unity. This indicates that the dependence upon hydrogen ion concentration may be represented by equation (4). Many reports have been made to the effect that the presence of excess acid inhibits the transition, but this plot indicates that this inhibition comes about by repressing the hydrolysis of the dichlorotetraquochromium(III) ion.

In order to calculate k_3 for the concentrations other than 25° it was necessary to determine the hydrolysis constant of green chromium(III) chloride at the other temperatures. This was done roughly by determining the pH of fresh solutions at the temperatures in question and using the method of Lamb and Fonda[9] to calculate the equilibrium constants. The values determined were: at 17.2° $K = 1.0 \times 10^{-6}$, at 35.8° $K = 4.3 \times 10^{-6}$.

Table II gives the average values of the specific reaction rate constants determined.

TABLE II

Temperature, °C.	Constants
17.2	2.3×10^{-2}
25.0	$4.57 \times 10^{-2} \pm 0.12^{a} \times 10^{-2}$
35.8	10.3×10^{-2}

[a] Standard deviation of the mean.

A plot of the logarithm of the values of k_3 against the reciprocal of the absolute temperature was made and the points were found to fall on a straight line. From this plot the activation energy was calculated to be 13,300 calories per mole.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Oxidation of Lithium and the Alkaline Earth Metals in Liquid Ammonia

BY JOSEPH K. THOMPSON AND JACOB KLEINBERG

Solutions of the metals (lithium, calcium, strontium, and barium) were rapidly oxidized by two methods, which are designated as the "one-cell method" and the "two-cell method." The former consisted of oxidation by dropping the metal sample directly into oxygen-saturated liquid ammonia; whereas the latter method consisted of dissolving the metal in ammonia and then slowly passing this solution into a cell containing oxygen-saturated liquid ammonia so that oxidation was instantaneous. All the metals react to yield chiefly monoxide and small percentages of peroxide; no higher oxides are found in the products. All the metals yield small amounts of amide as indicated by the presence of nitrite in the oxidation products. In the case of the alkaline earth metals the products contain traces of unreacted metal as shown by the evolution of hydrogen upon addition of water. Lithium, when rapidly oxidized in liquid ammonia at −78°, forms a bright lemon-yellow solution. Measurements of the absorption spectra of oxidized solutions of lithium, sodium and potassium show that all have absorption bands reasonably close to the same wave length, 380 mμ. Since sodium and potassium are known to form superoxides upon rapid oxidation in liquid ammonia, the similarity of their absorption spectra with that of lithium supports the postulate that the latter forms a superoxide which is stable in liquid ammonia solution at −78°. Electrolysis of magnesium bromide in liquid ammonia between a magnesium anode and a platinum cathode yields blue solutions of the ionized metal. Oxidation of such solutions results in the formation of small amounts of peroxide; faint, but positive tests for nitrite are also obtained.

The literature on the oxidation of liquid ammonia solutions of lithium and the alkaline earth metals is scanty. Pierron[1] reported a 23% yield of peroxide when oxygen is bubbled through solutions of lithium in liquid ammonia. Guntz and Mentrel[2] reported the formation of gelatinous mixed oxide precipitates containing 7–9% peroxide when barium is treated similarly.

The oxidation in liquid ammonia of the alkali metals other than lithium has been thoroughly studied.[3] According to Kraus and Whyte[4] slow oxidation of potassium, and presumably of sodium also, results in the initial formation of peroxide which is reduced by excess metal to the monoxide. Ammonolysis of the latter yields amide which is subsequently oxidized to nitrite. Rapid oxidation of potassium produces chiefly the peroxide, provided the process is interrupted as soon as free metal disappears; the peroxide may then be converted to superoxide by continued oxidation. There is practically no amide formation when potassium is rapidly oxidized at −50°.[5] Schechter, Thompson and Kleinberg[6] have demonstrated that amide formation can be avoided during the rapid oxidation of sodium only under carefully controlled conditions. The purpose of the work described in this report was to study the behavior of lithium and the alkaline earth metals under the conditions which inhibited amide formation in the case of sodium.

Experimental

Method of Oxidation.—Solutions of lithium and the alkaline earth metals were oxidized by two methods, which will be designated as the "one-cell method" and the "two-cell method." The apparatus used was essentially the same as that designed and used by Schechter, Thompson and Kleinberg[6] in their studies on the oxidation of sodium in liquid ammonia. In the "one-cell method" the sample of metal was dropped into a cell containing about 75 cc. of liquid ammonia (refrigeration grade) through which dry oxygen was bubbling at a rate of about 40 cc. per minute. In the "two-cell method" the metal sample was dissolved in about

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[1] P. Pierron, *Bull. soc. chim.*, [5] **6**, 235 (1939).

[2] A. Guntz and Mentrel, *ibid.*, [3] **29**, 585 (1903).

[3] G. W. Watt, *Chem. Revs.*, **46**, 293 (1950).

[4] C. A. Kraus and E. F. Whyte, THIS JOURNAL, **48**, 1781 (1926).

[5] C. A. Kraus and E. F. Parmenter, *ibid.*, **56**, 2384 (1934).

[6] W. H. Schechter, J. K. Thompson and J. Kleinberg, *ibid.*, **71**, 1816 (1949).

40 cc. of ammonia in one cell, and then the solution was passed slowly into the second cell which contained about 75 cc. of liquid ammonia through which dry oxygen was bubbling at a rate of about 40 cc. per minute. The solution was passed slowly enough that no blue color persisted in the second cell; the metal was oxidized immediately as the solution entered the oxidation cell. The samples of metal, a few milliequivalents in weight, were cut and scraped in a dry-box and then transferred to the cell in glass capsules which fitted into the cell by means of ground glass joints.[7]

Method of Analysis.—After oxidation was complete by either method, the ammonia was allowed to evaporate, and the residue was analyzed. Analysis for peroxide consisted of catalytic decomposition of the product with manganese dioxide suspension and measurement of the volume of oxygen evolved, followed by titration of the dissolved residue with standard acid to determine the total base content. The evolved gas was ignited to determine the amount of hydrogen from the reaction of unoxidized metal with the catalyst suspension. The dissolved residue was tested for nitrite by means of a spot test involving the dye formation between α-naphthylamine and sulfanilic acid in the presence of nitrite.[8] Since the products contained a yellow material, it was concluded that no superoxide was present.

Absorption Spectra Measurements.—Absorption spectra measurements were made at −78° on liquid ammonia solutions of the oxidation products of lithium, sodium and potassium with a Coleman Model 11 Universal Spectrophotometer which had been modified to accommodate liquid ammonia solutions. The conversion was accomplished by substituting a quartz Dewar flask and absorption cell similar to those described by Gibson and Argo[9] for the conventional absorption cell and carrier.[10] No change was made in the optical or electrical system of the instrument. In using this instrument it was necessary to measure the apparent transmission (indicated by the galvanometer reading) over the entire wave length range separately for solvent and solution. At any particular wave length the difference between the transmission of the solvent and that of the solution divided by the transmission of the solvent gives the absorption of the solution. Multiplication of this quantity by 100% gives the % absorption of the solution.

Results and Discussion

Oxidation Studies.—Lithium dissolves readily at temperatures near −33° to form a deep blue solution. There is no evidence that an insoluble phase is formed at such temperatures. Oxidation of the blue solution at this temperature by either the "one-cell method" or the "two-cell method" gives a milky-white suspension, which subsequently turns light yellow in color. As the ammonia evaporates, a white residue is left.

Lithium does not dissolve readily in liquid ammonia at −78°, but the metal can be oxidized at this temperature by dropping the sample into liquid ammonia through which oxygen is bubbling. The metal gradually dissolves, becoming oxidized immediately upon solution. No intermediate blue solution of metal is formed. The color of the solution after oxidation at this temperature is a bright lemon-yellow. When the solution is permitted to warm up toward −33°, the yellow color fades, giving way to a white suspension. The color cannot be brought back by cooling the cell again. Whether the metal is oxidized at −33 or −78°, the product after evaporation of the ammonia is the same white flaky substance. Studies of the absorption spectra of these solutions and their implications will be discussed later.

Calcium does not dissolve appreciably when placed in liquid ammonia at −78°. At −33° the metal is readily soluble, forming blue solutions which separate into two liquid phases of approximately the same density. Oxidation of these solutions gives a white or gray residue.

The behavior of strontium with regard to its solubility in liquid ammonia is identical with that of calcium. Oxidation gives a white suspension; the product after evaporation of the ammonia is a gray powder.

Barium dissolves the most readily of the three alkaline earth metals, forming the usual deep blue solution. When the metal is added to ammonia at −78°, there appear to be two liquid phases; but as the temperature is raised, the solution becomes homogeneous. Oxidation of this solution gives the usual white suspension. The product after evaporation of the ammonia is always a gray powder.

The results of the oxidation studies are summarized in Table I. Lithium and the alkaline earth metals behave nearly alike when oxidized in liquid ammonia. The product in every case contains chiefly monoxide and a relatively low percentage of peroxide. This behavior is to be contrasted with that of the other alkali metals, all of which give high percentages of superoxide when oxidized under these conditions. It must be pointed out that monoxide is probably not formed by any process other than that of direct oxidation. The mechanism for monoxide formation found for potassium, namely, reduction of peroxide by metal,[4] would not appear to apply here since essentially the same quantity of monoxide is obtained in both the "one-cell" and "two-cell" methods of oxidation. In the latter method there is never any excess of metal in the solution being oxidized and consequently no possibility for reduction of peroxide.

TABLE I

PRODUCTS FOUND AFTER OXIDATION OF LITHIUM AND THE ALKALINE EARTH METALS IN LIQUID AMMONIA AT −33°

	One-cell oxidation			Two-cell oxidation		
Metal	Peroxide, %	Nitrite, %	Unreacted, metal, %	Peroxide, %	Nitrite, %	Unreacted metal, %
Lithium	26 ± 6 (17 runs)	5	0.5	26 ± 6 (23 runs)	5	0.5
Calcium	12 ± 2 (8 runs)	3–10	1	12 ± 2 (6 runs)	3–10	1
Strontium	20 ± 2 (5 runs)	4	2	25 ± 3 (6 runs)	4	2
Barium	37 ± 6 (9 runs)	4	8	25 ± 5 (7 runs)	2	1

The tendency to form peroxide in the alkaline earth group increases in the order of increasing

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(7) A few exploratory tests were made with magnesium. It was not possible to get magnesium into solution directly, but it was found that, when solutions of magnesium bromide in liquid ammonia were electrolyzed between a platinum cathode and a magnesium anode, blue solutions of ionized metal were formed. This behavior was quite analogous to that described for aluminum in a previous report from this Laboratory (A. W. Davidson, J. Kleinberg, W. E. Bennett and A. D. McElroy, THIS JOURNAL, **71**, 377 (1949)). The products of oxidation of such solutions of magnesium gave positive qualitative tests for peroxide and for nitrite. Quantities were too small for any quantitative determinations to be made.

(8) F. Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publishing Company (Elsevier-Amsterdam), New York, N. Y., 1937, p. 203.

(9) G. E. Gibson and W. L. Argo, THIS JOURNAL, **40**, 1327 (1918).

(10) The authors are indebted to Mr. R. R. Miller, of the Naval Research Laboratory, Washington, D. C., for the loan of these quartz items.

ionic size. This order is only qualitative, and it should not be inferred that a direct proportionality exists. Lithium, which is smaller than any of the alkaline earth metals, does not fall into such an order on the basis of ionic size alone.

The tendency for unreacted metal to appear in the product of oxidation increases with increasing ionic size. This is true especially in runs made by the "one-cell" method. There is little evidence of unreacted metal in the products of "two-cell" runs.

Oxidation by either the "one-cell" or the "two-cell" process gives about the same yield of peroxide for lithium and calcium. For strontium the "two-cell" process gives slightly higher amounts than the "one-cell" process. For barium, on the other hand, the latter method gives greater yields than the former. No explanation can be offered for these variations.

In every case the oxidation product contains nitrite equivalent to a few per cent. of the total metal used. This fact indicates that there is a strong tendency for amide formation to occur. One source of amide formation may be the ammonolysis of monoxides, as described by Kraus and Whyte[4]; another source[11] may be the decomposition of ammoniates according to the equation

$$M(NH_3)_6 \longrightarrow M(NH_2)_2 + H_2 + 4NH_3$$

The exact mechanism of nitrite formation is unknown and is worthy of further investigation.

Absorption Spectra Studies.—It has been previously mentioned that lithium is oxidized at −78° to form a lemon-yellow solution. Sodium and potassium give yellow solutions in which some solid yellow matter is suspended. The color of the solutions is less intense than that formed from lithium due to limited solubility of the superoxides. Absorption studies were made on oxidized solutions of lithium, sodium and potassium after filtration of solid matter. The % absorption of the solutions relative to the pure solvent is shown in the graph in Fig. 1.

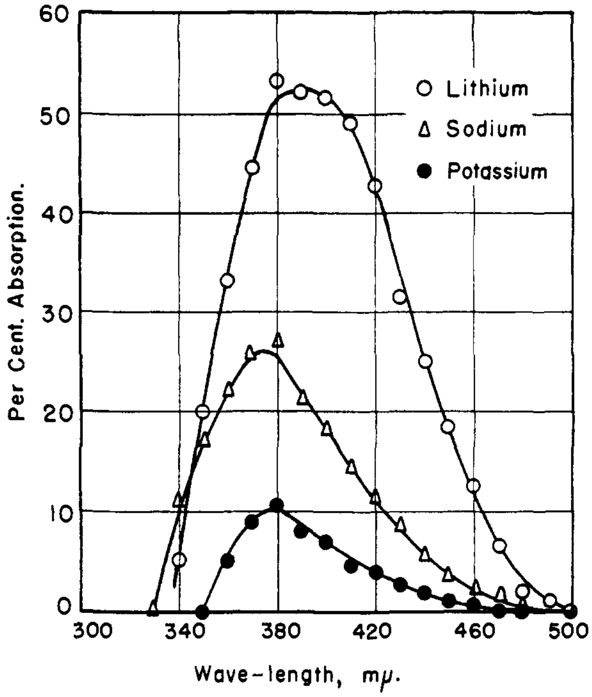

Fig. 1.—Absorption spectra of products of oxidation of alkali metals in liquid ammonia.

Comparison of the absorption curves in the graph shows that in every case the solution has an absorption maximum in the violet region of the spectrum. When allowance is made for the 35 mμ band width of the instrument, the maxima in the absorption curves appear to occur reasonably close to the same wave length, 380 mμ. The relative heights of the absorption maxima decrease in the order lithium, sodium and potassium. Though no quantitative measurement of solubility was made, this order appears to be that of decreasing solubility of the substance responsible for the absorption. Since sodium and potassium are known to form superoxides upon rapid oxidation in liquid ammonia, the similarity of these absorption spectra supports the postulate that lithium forms a superoxide which is stable in liquid ammonia solution at −78°.

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[11] E. Botolfsen, *Bull. soc. chim.*, [4] **31**, 561 (1922).