

Studies on Lithium Acetylide

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In contrast to the large amount of work done on the acetylene derivatives of sodium, potassium and calcium, little attention has been paid to the analogous compounds of lithium. In 1898 Moissan¹ prepared lithium acetylide on a small scale, by the action of acetylene on a liquid ammonia solution of lithium. He reported that lithium acetylide was less soluble in liquid ammonia than sodium acetylide, and that when isolated from the solvent, it was less stable, undergoing decomposition with evolution of acetylene. On the basis of the weight of lithium acetylide obtained from a given weight of lithium, and from the amount of acetylene liberated on hydrolysis, he assigned to lithium acetylide the formula $C_2Li_2 \cdot C_2H_2 \cdot 2NH_3$. Since that time no references to lithium acetylide or lithium alkylacetylides have appeared in the literature. It was the purpose of the present work, therefore, to prepare and analyze lithium acetylide and a lithium alkylacetylide, and to compare their reactions with those of the better known sodium derivatives.

Experimental Procedure

Preparation of Lithium and Sodium Acetylides.—Acetylene gas, washed by bubbling through concentrated sulfuric acid, was passed into two liters of liquid ammonia, while 7 g. (1 mole) of metallic lithium, cut in small pieces, was added gradually, with stirring, at a rate such that the solution did not develop a permanent deep blue color. When the solution became colorless after the addition of the last piece of lithium, the flow of acetylene was stopped. Sodium acetylide was made in the same way from 23 g. of sodium. The alkali acetylides so prepared were used immediately, without isolation.

Reaction of Sodium and Lithium Acetylides with n-Amyl Bromide.—One mole of n-amyl bromide (151 g.) was added during half an hour, to a freshly prepared solution of lithium acetylide made from 7 g. of lithium. The reaction mixture was stirred for 2.5 hours, and was then hydrolyzed by the addition of ammonium hydroxide and water. The organic layer was washed with water, dilute hydrochloric acid, and 10 per cent sodium carbonate solution, and was dried over magnesium sulfate. The product was then fractionated through a Vigreux column. The reaction of sodium acetylide with n-amyl bromide was carried out in exactly the same way, using the same number of moles of reactants. Duplicate runs were made with each acetylide.

Reaction of Sodium and Lithium Acetylides with Methyl Ethyl Ketone.—Lithium and sodium acetylides were prepared as described

¹ Moissan, 1898. *Compt. rend.*, **127**:911.

above, and 73 g. (1 mole) of methyl ethyl ketone was added to each solution, with stirring, over a period of forty minutes. The reaction mixtures were stirred for three hours, and the liquid ammonia was allowed to evaporate through a potassium hydroxide tower. The residue in each case was hydrolyzed at 0° with ice and 50 per cent sulfuric acid, the organic layer was washed with brine, dried over magnesium sulfate and distilled through a Vigreux column. Duplicate runs were made.

Analyses on Lithium Acetylide.—Lithium acetylide for analysis was made from 1 g. of lithium, 300 cc. of liquid ammonia and carefully-dried acetylene. Care was taken to exclude moisture during the preparation, and when the reaction was complete, the liquid ammonia was allowed to evaporate through a potassium hydroxide tower. The alkalimetry determinations were made by adding 10 ml. of dioxane to a weighed sample, to prevent explosion, and then adding 70 ml. of water. The base liberated was titrated to the methyl-orange end point with 0.4 N. hydrochloric acid. In the determinations of lithium as lithium sulfate a sample of the acetylide was gently heated in a porcelain crucible, with a direct flame, until decomposition was complete. The residue was moistened with concentrated sulfuric acid and the crucible was finally heated to dull redness. The alkalimetry and lithium determinations were carried out on four successive days to follow the decomposition of the substance. Since lithium acetylide gradually decomposes on standing, with liberation of acetylene, it cannot be stored in a closed weighing bottle. It was kept in an open flask, protected from moisture by a potassium hydroxide tower.

Thermal decomposition of lithium acetylide.—Weighed samples were heated in a current of nitrogen, and the emerging gases were passed through standard sulfuric acid to absorb ammonia and then through silver nitrate solution to absorb acetylene. The excess sulfuric acid in the first wash-bottle was determined by titration to the methyl-red end-point, and the nitric acid liberated in the silver nitrate solution was also determined by titration. The weight of the residue was obtained, and the residue was then decomposed with dioxane and water, and the alkalinity of the solution determined by titration.

Solubilities of lithium and sodium acetylides.—Liquid ammonia was allowed to evaporate from a solution of the alkali acetylide until the acetylide began to precipitate, and the volume of the solution was noted. Liquid ammonia was then added until solution was again complete, and the volume again noted.

TABLE I.—Yields of Products from Lithium and Sodium Acetylides

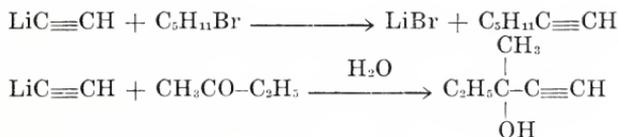
Product	B.pt.	Per Cent Yield from Lithium Acetylide	Per Cent Yield from Sodium Acetylide
n-Amylacetylene	97-100*	67.5	65
Methylethylethynylcarbinol	61°/70 mm.	59	65

Lithium n-amylacetylide.—One-half mole of lithium (3.5 g.), cut in small pieces, was added gradually to 500 ml. of liquid ammonia containing a small amount of ferric nitrate. To the lithium amide solution so prepared 55.8 g. of n-amylacetylene was added gradually. The lithium n-amylacetylide was then treated, without isolation, with 0.5 moles of n-amyl bromide, added over a period of forty minutes. The reaction mixture was stirred for thirty minutes, and then hydrolyzed with ammonium hydroxide and water. The organic layer was washed, dried, and distilled in the usual way, and gave a 60 per cent yield of di-n-amylacetylene.

The liquid ammonia was allowed to evaporate (through a drying tower) from one portion of lithium n-amylacetylide, and weighed samples of the residue were decomposed with dioxane and water, and the base formed determined by titration.

Discussion of Results

The results obtained in this work indicate that lithium acetylide is stable in liquid ammonia solution, and probably has the formula $\text{LiC}\equiv\text{CH}$, since it reacts normally with alkyl halides and ketones to give the expected products.



From the data in Table I it will be seen that these products are obtained from lithium acetylide in substantially the same yields as they are from sodium acetylide. No evidence was obtained for the presence in the products of any di-amylacetylene or dimethyl-diethyl-butynediol, which would be formed if any appreciable amounts of lithium carbide, Li_2C_2 , were present in the liquid ammonia solution.

In contrast to the report of Moissan, we found that lithium acetylide is more soluble in liquid ammonia than is sodium acetylide, since 1 liter of liquid ammonia was required to dissolve one mole of lithium acetylide, whereas 1300 cc. were required for one mole of the sodium salt.

Lithium acetylide appears to undergo spontaneous decomposition with liberation of acetylene, during its isolation from liquid ammonia, since the substance immediately after isolation contains 32% of lithium, whereas lithium acetylide, LiC_2H , should contain but 21.7% of lithium. There is probably no appreciable ammonia of solvation, since the amount of base formed on hydrolysis can be substantially accounted for by the amount of lithium present. The analytical results are summarized in Table II.

TABLE II.—Analyses on Lithium Acetylide

Time After Isolation	Equiv. of a Base per g.	Equiv. of b LiOH per g.	Per Cent of Li.
One day	0.0463	32.4
Two days	0.0445	0.0428	30.0
Three days	0.0448	0.0428	29.95
Four days	0.0449	0.0407	28.5
Calc'd. for $\text{Li}_2\text{C}_2\text{H}$:	0.0312	21.7
Calc'd. for $\text{Li}_2\text{C}_2\text{C}_2\text{H}_2\cdot 2\text{NH}_3$:	0.0408	14.2
Calc'd. for Li_2C_2 :	0.0527	36.6
Calc'd. for $\text{Li}_2\text{C}_2\text{LiC}_2\text{H}$:	0.0428	29.8

(a). Total basicity as determined by titration.

(b). Equivalents of LiOH per g. as calculated from the per cent of Li found.

These results show definitely that Moissan's formula for lithium acetylide is erroneous, but they do not permit us to postulate a definite formula for lithium acetylide. On the basis of the evidence presented, the most plausible explanation is that lithium acetylide decomposes to an approximately equimolar mixture of lithium acetylide and lithium carbide, and that there is some ammonia vapor occluded, in the first few days, at least. As this gradually diffuses out, and is replaced by air, partial oxidation occurs, with consequent decrease in the per cent of lithium. Calcium and barium acetylides have been shown to undergo similar decomposition to complexes of the carbides.

When lithium acetylide was heated at 150° in an atmosphere of nitrogen for thirty minutes a small amount of ammonia was evolved, and a still smaller amount of acetylene, and the residue increased in lithium percentage. When the substance was heated at 100° for two and a half hours, only a trace of acetylene was liberated, together with a little ammonia. These results indicate that ammonia of occlusion is driven off fairly easily, but that the approximately equimolar mixture of lithium acetylide and lithium carbide does not readily liberate much acetylene to form a mixture richer in the carbide.

In contrast to lithium acetylide, lithium n-amylacetylide is stable both in liquid ammonia solution and when isolated. In liquid ammonia solution it reacts normally with amyl bromide to give the expected di-n-amylacetylene. Analysis of the isolated salt by titration showed it to contain 6.35% of lithium, whereas the percentage of lithium in a compound of the formula $\text{LiC}\equiv\text{C}-\text{C}_5\text{H}_{11}$ is 6.8%

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Summary

1. Lithium acetylide has been prepared in liquid ammonia solution, and shown to react normally with alkyl halides and ketones.

2. Lithium acetylide decomposes on isolation from liquid ammonia. Analyses show that the formula $\text{Li}_2\text{C}_2\text{C}_2\text{H}_2\cdot 2\text{NH}_3$, suggested by Moissan, is erroneous, and that probably the substance when isolated from liquid

ammonia decomposes to an approximately equimolar mixture of lithium acetylide and lithium carbide.

3. Lithium n-amylacetylide has been prepared and shown to react normally with alkyl halides. It is stable when isolated from liquid ammonia solution.