labeled compound, or for transfer to a gas activity measuring device such as an ionization chamber or gas counter, it has been common practice to drop either concentrated phosphoric or sulfuric acid on the $BaCO_3$.[3] This procedure often involves the use of a stopcock in contact with concentrated acid, does not permit the ready attainment of high vacuum and may entail the formation of a crust of insoluble barium sulfate or phosphate around the active barium carbonate. In practice a still more disconcerting factor has been the spattering of the dry powder on contact with acid with the consequent sweeping of a portion of the sample out of the reaction vessel by the evolving gas. The direct thermal evolution of the C^*O_2 from BaC^*O_3 by roasting the dry salt in a quartz tube has also been used[4] but the temperature necessary is inconveniently high.

These difficulties may be surmounted by using a thermal reaction between dry solids to evolve the carbon dioxide. Acids such as potassium bisulfate are unsuitable as the reaction will produce water as well as carbon dioxide. Inorganic acid anhydrides such as boric oxide and the pyro salts melt at too high a temperature to be used in Pyrex apparatus. Organic anhydrides sublime under vacuum. A convenient reaction, however, is a metathetic one producing a thermally unstable carbonate such as the reaction between barium carbonate and lead chloride. Lead chloride was used because it can be readily obtained in an anhydrous state, and has a low melting point and vapor pressure. Silver chloride can also be used.

To obtain the total carbon dioxide from a barium carbonate sample, two procedures have been worked out. In the micro-procedure the weighed barium carbonate, from 5 to 200 mg., is dropped into a Pyrex test-tube with attached ground joint. Over this is layered 5 to 10 times its weight of dry powdered lead chloride, and then a wad of glass wool is pushed down on top. After attaching the tube to the vacuum system and pumping at 100°, the carbon dioxide is released by carefully melting the lead chloride with a micro burner. The reaction is known to be at least 98% complete from gas buret and activity measurements. The fusion temperature may be lowered by using a 50–50 mixture of $PbCl_2$–AgCl instead of pure lead chloride. The melt should not fill a full diameter of the reaction vessel or the latter may crack on cooling. For macro-quantities we have employed the following procedure. The two solids, one part by weight of barium carbonate and six parts by weight of lead chloride, were intimately mixed and ground together before placing the mixture in a reaction tube. The latter was connected to a standard vacuum system by means of a stopcock and a standard taper ground glass joint. The reaction mixture was pumped overnight at room temperature to a pressure of 10^{-5} mm. A tubular woven glass heating mantle was used as a heat source and the temperature was controlled by a Variac. Evolution of gas began at about 180° and each increment of temperature caused a more rapid evolution of gas which gradually decreased with time. It was found that the most convenient procedure was to raise the temperature to 400° as rapidly as possible (about twenty-five minutes) and maintain the reaction mixture at this temperature. The evolution of carbon dioxide was 65% complete in one hour from the start of heating, 80% in two hours and 96% complete in four hours. 3–9 g. of barium carbonate was employed in these experiments. Thus this reaction has been found to proceed at temperatures well below the fusion temperature and the system may therefore be used as a convenient, clean, "virtual" source of active carbon dioxide.

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RECEIVED AUGUST 16, 1948

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[3] (a) W. G. Dauben, J. C. Reid and P. E. Yankwich, *Ind. Eng. Chem., Anal. Ed.*, **19**, 828 (1947); (b) J. T. Kummer, THIS JOURNAL, **69**, 2239 (1947); (c) J. L. Huston and T. H. Norris, *ibid.*, **70**, 1968 (1948).

[4] M. G. Inghram, Atomic Energy Commission, MDDC 60, June, 1946.

COMMUNICATIONS TO THE EDITOR

METALLIC ALUMINUM IN SOLUTION IN LIQUID AMMONIA

Sir:

It has long been generally accepted that the alkali metals, in dissolving in liquid ammonia, dissociate into alkali metal cations and free (solvated) electrons,[1] and that the latter impart the characteristic blue color to such solutions. The alkaline earth metals are known to dissolve similarly, although to a smaller extent.[2] Makishima[3] included the dissolution of electrons among electrode reactions which may occur at a cathode in liquid ammonia solutions, and Laitinen and Nyman[4] have very recently pointed out that, theoretically, all metals should be in some degree soluble in liquid ammonia. According to the hypothesis

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(1) Kraus. THIS JOURNAL. **30**, 1323 (1908).

(2) Kraus, *ibid.*, **30**, 660 (1908).

(3) Makishima, *J. Faculty Eng. Tokyo Imp. Univ.*, **21**, No. 3, 115 (1938).

(4) Laitinen and Nyman. THIS JOURNAL, **70**, 3002 (1948).

of these latter authors, however, the solubility of metals less active than calcium should be exceedingly small.

On the basis of the reaction of metallic aluminum with solutions of alkali metal amides in liquid ammonia, Bergstrom[5] postulated that aluminum must be soluble in this solvent to a slight extent. There is no record in the literature, however, of any actual observation of a blue solution of metallic aluminum in ammonia, although Booth and Merlub-Sobel,[6] in a study of the electrolysis of aluminum iodide, reported the formation at the cathode of a transitory blue-black film which they suggested might be a subiodide or subnitride of aluminum.

In the course of an investigation, recently begun in this Laboratory, of the anodic oxidation of aluminum in solutions of various salts in liquid ammonia, we have carried out several electrolyses with aluminum iodide as electrolyte. In every such case, we have observed the appearance, in the immediate vicinity of the *cathode*, of a deep blue color. This color is at first impermanent, disappearing upon diffusion into the body of the solution with the concurrent formation of a white precipitate, and being regenerated at the cathode. On prolonged electrolysis, however, the rate of disappearance gradually decreases, and the entire solution eventually becomes dark blue. The most striking results were obtained in a solution containing 0.3 g. of aluminum iodide in 48 g. of ammonia, which was electrolyzed at −33° in an atmosphere of nitrogen between a bright platinum cathode and a chemically pure aluminum anode, at a cathode current density of about 0.01 amp. per sq. cm.

We are unable to account for these results in terms of any hypothesis other than the following. The cathode reaction appears to consist of the dissolution of electrons, which are able to exist in the presence of a considerable concentration of Al^{+++} ion. The blue solute, consisting therefore of ionized metallic aluminum, at first reacts rapidly with the solvent, liberating hydrogen and yielding an insoluble white derivative of aluminum amide; subsequently, however, the rate of this reaction decreases, so that an appreciable concentration of aluminum metal is able to persist in the solution for as much as fifteen minutes after the current is discontinued.

This phenomenon is being studied further, and will later be the subject of a more complete report.

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[5] Bergstrom, THIS JOURNAL, **45**, 2788 (1923); **46**, 1545 (1924); *cf.* Fernelius and Watt, *Chem. Revs.*, **20**, 195 (1937).

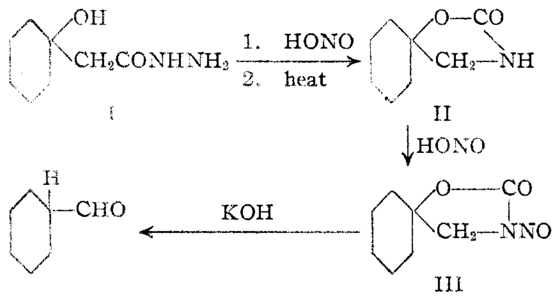
[6] Booth and Merlub-Sobel, *J. Phys. Chem.*, **35**, 3303 (1931)

A NOVEL REACTION IN ORGANIC CHEMISTRY

Sir:

In connection with studies designed to develop a new approach to ring enlargement of cyclic ketones, an interesting new reaction has been discovered. When 3-nitroso-1-oxa-3-azaspiro[4,5]-decan-2-one, III, is treated with alkali, nitrogen is evolved immediately and hexahydrobenzaldehyde is produced. This aldehyde has been isolated in over 50% yield as the semicarbazone,[1,2] m. p. 172–173° after sintering at 166°.

The nitroso compound was prepared by the following series of reactions



Further studies as to the generality and mechanism of this reaction are under way in this Laboratory.

The author wishes to acknowledge a grant from the Research Corporation which has greatly assisted in this work.

Hydrazide of 1-Cyclohexanolacetic Acid, I.—This compound, m. p.[3] 102.2–104.4°, was prepared in 78% yield.

Anal. Calcd. for $C_8H_{16}O_2N_2$: C, 55.8; H, 9.4; N, 16.3. Found: C, 55.6, 55.8; H, 8.9, 8.7; N, 16.3, 16.4.

1-Oxa-3-azaspiro[4,5]decan-2-one, II.—The hydrazide, I, was dissolved in dilute hydrochloric acid and treated with a slight excess of sodium nitrite at 10–15°. The reaction mixture containing the resulting oily azide was slowly heated to 45° when decomposition began. Rapid stirring and temp. control near 50° are necessary to prevent violent decomposition. The cyclic urethan,[4] II, was isolated in 82% yield as colorless crystals, m. p. 101.0–102.4°.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.9; H, 8.4; N, 9.0. Found: C, 61.8; H, 8.2; N, 9.3.[5]

On alkaline hydrolysis 1-aminomethylcyclohexanol (m. p. of N-benzoate,[6] 143–144°) was obtained.

3-Nitroso-1-oxo-3-azaspiro[4,5]decan-2-one, III.—II was converted into III, m. p. 82.8–83.2°, in 94% yield by nitrous acid.

Anal. Calcd. for $C_8H_{12}O_3N_2$: C, 52.2; H, 6.6; N, 15.2. Found: C, 52.3, 52.1; H, 6.3, 6.1; N, 15.5, 15.6.

Semicarbazide of Hexahydrobenzaldehyde.—To a solution of 1.84 g. of III in 15 cc. of alcohol was added drop-

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[1] Melting points ranging from 167° to 176° for this derivative have been reported in Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, 1925, 4th ed., Vol. VII, p. 20.

[2] The author wishes to thank Mr. Abraham Kutner for preparing authentic samples.

[3] All melting points corrected.

[4] A similar cyclization has been reported [Schroeter, *Frdl.*, **10**, 1309 (1910-12)] but no details are mentioned and analyses for the products were not reported.

[5] This analysis by H. S. Clarke, Microanalytical Laboratories, Urbana, Illinois. Other analyses by Mrs. E. H. Klotz, O.S.U.

[6] M. W. Goldberg and H. Kirchensteiner, *Helv. Chim. Acta*, **26**, 288 (1943).