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OXYCYANOGEN. I

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The field of inorganic free radicals contains, as is pointed out by Walden and Audrieth,¹ one piece of work, namely that of Lidov,² which must be substantiated or disproved before the properties of the radical CNO can be definitely established. Since no mention of Lidov's work is made by Birckenbach and Kellermann,³ I thought it advisable to check this work before proceeding farther into the field.

Lidov did not hint that the substance with which he was dealing was a free radical. All evidence offered by him for the existence of a substance composed of carbon, nitrogen and oxygen hinges on density determinations of a gas. No chemical composition is proved by analysis. The electronic structure of OCN shows it to have an odd electron and hence we would expect it to be very active chemically unless polymerized. That such is not true of Lidov's substance is apparent since he prepared it in aqueous or alcoholic solutions without hydrolysis. He described his product as being a homolog of carbon dioxide, and names it oxan or monocyan.

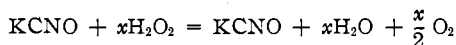
Oxan is described as being a gas which polymerizes on standing, yet Lidov never obtained a greater density than 1.974 g./l. It is not decomposed by phosphoric acid or by temperatures up to 375°. It is precipitated by silver or barium ion and absorbed by an alkali. By long boiling with sodium hydroxide and zinc dust its salts will give ammonia. The nitrogen of beta-oxan is easily determined by burning it with magnesium powder.

The greatest care was taken to repeat most of Lidov's work, even in the most illogical cases, in order that I might definitely say that his work was correct or incorrect. The detailed results are as follows.

Paper Number 1.—A. In neutral solution, aqueous or alcoholic



The oxanate, K_2CNO_2 , may be decomposed with phosphoric acid to give CNO also. The author found the following



The effluent gas supports combustion and is absorbed completely by alkaline pyrogallol. No precipitate was obtained by passing the gas into

¹ Walden and Audrieth, *Chem. Reviews*, **5**, 339 (1928).

² A. P. Lidov, *J. Russ. Phys.-Chem. Soc.*, **44**, 527 (1909); **44**, 529 (1909); *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, **6**, 185, 191, 194 (1912); *THIS JOURNAL*, **35**, 132 (1913); *Rev. gén. chim.*, **16**, 293, 310 (1914); "Tech. Inst. Charkov," Russia (Monograph) (1914).

³ Birckenbach and Kellermann, *Ber.*, **58**, 786 (1925).

barium hydroxide solution. The remaining salt was then decomposed by phosphoric acid as described and the gas evolved passed into barium hydroxide. The precipitate was washed and then digested with potassium hydroxide and aluminum dust. Not a trace of ammonia could be detected with Nessler's solution. When the Kjeldahl method failed to give ammonia, I also failed to get any Mg_3N_2 formed by burning the gas with magnesium.

B. In alkaline solution, aqueous or alcoholic



I repeated this reaction, in a closed vessel, in dry, cold alcoholic solution. The hydrogen peroxide was added slowly but oxygen was persistently given off. The concentrated solution was decomposed with phosphoric acid. The resulting gases were passed into barium hydroxide solution. The barium salt was then boiled with aluminum dust in strong alkali, but no trace of ammonia was given off (Nessler test). Therefore it is quite evident that the evolving gases are carbon dioxide and nitrogen and not CNO. Lidov's trouble of having an extra amount of barium salt precipitated in the reaction flask, which he calls $BaCNO_3$, would have been overcome if he had allowed the gas to escape and pass into barium hydroxide solution instead of trying to precipitate the effluent gas in the reaction flask.

Paper Number 2.—(See part 5 of Number 3.)

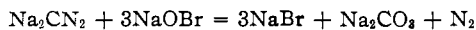
Paper Number 3.—A. Lidov claims that the familiar reaction



is not correct but that as we increase the dilution of the solution (alcoholic), we have more and more CNO formed. He supports this assumption by the meager evidence that he did not find the theoretical amount of carbon dioxide formed but a gas weighing (1.974, 1.945, 1.925, 1.921 and 1.911) g. per liter. "Further dilution, however, does not bring near the weight of the gas and the weight of a liter of pure oxan—1.875 g."

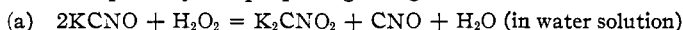
This titration was carefully repeated and the gases formed passed into barium hydroxide. The precipitate was tested for nitrogen content in the usual manner and was found to contain none.

B. Sodium cyanamide was claimed to give oxan on oxidation with hydrogen peroxide (perhydrol) or sodium hypobromite, very small quantities of nitrogen being liberated. However, I found the reactions to proceed as follows in aqueous solution

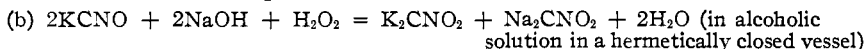


If the cyanamide or a cyanate is converted to an ammonium compound the strong oxidizing agents will oxidize it to free nitrogen, reducing agents giving ammonia. The sodium salts left were decomposed and the gas evolved proved to be pure carbon dioxide.

C. Other simple ways of preparing the gas are



"There is always more or less potassium carbonate and ammonium carbonate formed," Lidov reports.



"No nitrogen is expelled and 15–20% extra Ba salt is precipitated." In checking these experiments I obtained the same results as described in paper I.

D. In this section properties of oxan salts are given. Lidov obtained his oxan salts, BaCNO_2 , K_2CNO_2 , etc., as shown in reactions above, but I was unable to separate any new salts.

E. By heating a mixture of KCNO and CuO to 375° in a stream of dry nitrogen, Lidov found



"That the reaction is really so, is confirmed as well by the weight of the gas expelled (1.900) by the heating, as by the weight of the gas produced from the remaining salts." I find the reaction to proceed as follows



when everything is carefully dried and protected from water vapor. Otherwise I find



The expelled gases in the former reaction were passed through barium hydroxide. No trace of nitrogen was found in the precipitate. No evidence of CNO_2 , or CNO_3 , as reported, was found. (No oxidizing salt was left in the tube.)

F. When Lidov used oxygen instead of nitrogen, as in V, he found $\text{KCNO} + \text{CuO} + \text{O}_2 = \text{K}_2\text{CNO}_2 + \text{CNO} + \text{CO}_2 + \text{Cu} +$ (a heavier gas, 2.590, precipitated with Ba^{++})

I found the simple conditions



which is in accord with all Dumas' determinations.

G. "Of the Formation of Oxan by the Reciprocal Action of Nitrogen Dioxide with Charcoal." Lidov learned in the following year that he was using nitric oxide and not nitrogen dioxide (see paper No. 6).

"The simplest way of obtaining oxan . . . if we judge by weight of the gas" is to pass NO (not NO_2) over charcoal at 150° . "If the solution of sodium hydroxide, which has absorbed the gas, is immediately decomposed by phosphoric acid, in most cases pure oxan, if we judge by weight, is obtained." I followed Lidov's explicit directions for the best method of getting the pure gas (see part VII of paper 3 and paper 6) and absorbed it in alkali as stated. It was then precipitated as the Ba salt and carefully

washed to get rid of any nitrates or nitrites. It was then decomposed by phosphoric acid, the evolved gas passed through a vapor trap and then through long tubes of phosphorus pentoxide and finally frozen out in a liquid air trap. The density of the gas was determined as described by Schumb and Gamble.⁴ The gas was found to have a density of 1.9693 g. per liter, which is within 0.4% of the determined density of carbon dioxide ("International Critical Tables," Vol. III, p. 1). The gas was allowed to stand for several days and its density determined at two-day intervals. No polymerization takes place as evidenced by the various determinations.

June.....	17	19	21	23	25
Density.....	1.9693	1.9693	1.9693	1.9693	1.9693

These latter experiments disprove Lidov's sole argument for the existence of a gas, CNO, homologous with CO₂.

Paper Number 4.—Since there is no evidence for the formation of the salts described in this paper by the given methods, I will not try to explain how he obtained the peculiar properties listed. Perhaps the compounds listed will have the properties described, but I have proved that such compounds cannot be prepared by the methods given.

Paper Number 5.—By passing nitrogen dioxide over charcoal at room temperature and collecting the gas in alcoholic sodium hydroxide, Lidov did not obtain oxan but beta-oxan, ONC. In repeating this work with carefully prepared gases and solutions, and pure dry sugar charcoal, I obtained a mixture of C₂H₄NaNO₂, NaNO₂ and Na₂CO₃, the two former occurring in the first few hours of reaction and the last after fifteen to twenty hours. My organic salt was identified by its reactions and properties identical to those listed for C₂H₄NaNO₂. The mixture on decomposition gave no gas of the nature of CNO, only oxides of nitrogen and carbon. The first-named compound will explain the explosive properties of beta-oxan salts.

Paper Number 6.—The foregoing experiments show that Lidov was dealing with impure carbonates in this paper, and not new compounds. By treating the solution mixture described in Paper 5 with ferric chloride, Lidov obtained a ferric salt which he called iron beta-oxanate. I found simply ferric hydroxide, the explosive properties being due again to C₂H₄NaNO₂.

Passing pure nitrous oxide over charcoal at 150° gave only carbon dioxide and nitrogen and not CNO as claimed by Lidov.

Paper Number 7.—A review of previous work with a few new methods of preparing oxan, such as heating phosphorus pentoxide and urea.

Papers Number 8 and 9.—To confirm the contents of these two papers, namely, that CNO is a product of all combustions in air along with carbon dioxide and carbon monoxide, and of respiration of animals, would prove all

⁴ Schumb and Gamble, THIS JOURNAL, 52, 4302 (1930).

Dumas' determinations inaccurate and calorific values subject to error. It would proclaim a new property of nitrogen, which has been proved not to be possible by thousands of able chemists, namely, the ability to support combustion. Therefore I wish to point out the fallacies of Lidov's writings.

Summary

1. The author has shown that $(\text{CNO})_x$ cannot be obtained by any of the methods described by Lidov.

2. He has proved that salts, such as Na_2CNO_2 , $\text{Fe}(\text{NCO})_3$ or BaCNO_2 , cannot be prepared as described.

3. He has shown that Lidov's peculiar observations are due to inaccurate work. This is particularly true of the density determinations.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]
ELECTRIC MOMENT AND MOLECULAR STRUCTURE. IV. THE GLYCOLS

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In the first paper¹ of this series the effect upon the resultant electric moment of the molecule produced by separating the component moments by a carbon chain of varying length was investigated, the complex $-\text{CO}-\text{OC}_2\text{H}_5$ group being placed at each end of the chain. In the present investigation the simpler $-\text{OH}$ group has been attached to the carbon chain. The low solubility of the glycols in the non-polar liquids, benzene and heptane, usually used as solvents in the determination of electric moments, has made it desirable to use 1,4-dioxane, which has been employed by Williams for a similar purpose.² Williams found values for the moments of chlorobenzene, chlorocyclohexane, diethyl *o*-phthalate, and water measured in dioxane in good agreement with the values obtained in other ways. It was feared, however, that the glycols might form addition products with the dioxane which would lead to incorrect values for the moments. In order to test the possibility of such errors, *n*-butyl alcohol, which had been thoroughly investigated in the vapor state³ and in solution in other solvents,⁴ was measured in dioxane. The monohydric alcohol would be expected to resemble to some extent, at least, the glycols in the possible formation of addition products and, therefore, in the error in the moment arising from such formation. The resemblance should be close in the case of the long-chain glycols.

¹ Smyth and Walls, *THIS JOURNAL*, **53**, 527 (1931).

² Williams, *ibid.*, **52**, 1838 (1930).

³ Miles, *Phys. Rev.*, **34**, 964 (1929).

⁴ Smyth and Stoops, *THIS JOURNAL*, **51**, 3312 (1929).