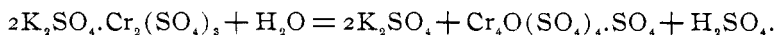


and  $\text{SO}_4$  in the basic chromium sulphate from Miller's analysis, there can no longer be any reason for not accepting the equation given for the change :



The conclusion drawn in the article by Miller and myself was conservative and still stands ; namely, that the color of the green solutions was due to the formation of basic salts of chromium, green and uncrystallizable, thus confirming the explanation first suggested by Berzelius. To this must now be added that this formation is accompanied by the liberation of a portion of the combined acid, in the case of the alum corresponding to one-half of the total.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 18].

## ON THE DECOMPOSITION OF NICKEL CARBONYL IN SOLUTION.

BY VICTOR LENHER AND HERMANN A. LOOS.

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IT has been shown by Berthelot that nickel carbonyl in contact with moisture suffers decompositions of a more or less complex character. When nickel carbonyl is mixed with water according to Berthelot<sup>1</sup> there is formed a green compound which consists of hydrate of the oxide free from carbon. A portion of the nickel carbonyl at the same time escapes and is oxidized in moist air to a whitish compound. This same white compound Berthelot prepared in larger quantity by the slow oxidation with air and found it to contain 5.3 per cent. carbon, 53.3 per cent. nickel oxide ( $\text{NiO}$ ), and 40.1 per cent. water.

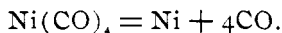
Mond<sup>2</sup> considers the green body formed when nickel carbonyl is exposed to damp air to be a carbonate of nickel of varying composition.

The deportment of nickel carbonyl in solution is different from that in the pure condition or as a gas, as is seen, for example, from the fact, that it will decompose in solution at  $60^\circ$ , whereas in the gaseous condition, it will not decompose until about  $150^\circ$ .

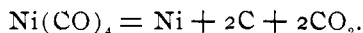
<sup>1</sup> *Compt. rend.*, **112**, 1343; **113**, 679.

<sup>2</sup> *Chem. News*, **64**, 108; also *J. Soc. Chem. Ind.*, **11**, 750.

In gaseous condition, heat decomposes it simply, into nickel and carbon monoxide.



In solution the action takes a different form and may be represented as follows :



It would not be surprising then to find that the solution would act differently than the pure substance, under the action of moisture or oxidation.

While working with nickel carbonyl dissolved in various organic solvents, such as chloroform, benzene, toluene, etc., it was found that the solutions on standing suffer decomposition with the formation of a green precipitate; this was probably due to the presence of more or less moisture, either in the solvent or in the surrounding atmosphere. That the precipitate is produced by the action of moisture is evidenced by the fact that the decomposition is more rapid when the solution is exposed to the air and still more rapid when moist air is bubbled through the solution.

A solution of nickel carbonyl will, after standing, suffer decomposition with the formation of a green to a brown gelatinous precipitate. In appearance, this precipitate is similar to that obtained by the action of water or moisture on pure liquid nickel carbonyl.

The precipitate formed from various solvents has been studied with a view of determining if possible its composition. The substance is evidently of very complex nature and is undoubtedly an oxidation product. When a solution of nickel carbonyl in acetone or chloroform is allowed to stand, a green gelatinous precipitate forms in a few hours. After a greater length of time the precipitation becomes complete, and on filtration, no nickel can be found in solution. This same decomposition takes place but more slowly in benzene, toluene, and methyl alcohol. The precipitate is colored light green to dark brown according to the solvent used, and according to the small amount of iron carbonyl which frequently contaminates the nickel carbonyl. The deportment of the solution in ethyl alcohol is peculiar. If this solution is mixed with an equal volume of water, a clear solution is

first obtained, but in a few minutes, it gelatinizes to a green translucent mass. This substance settles very slowly. On filtering off the precipitates and carefully drying, all assume a greenish color. Examination of this precipitate indicates that it is a decomposition product which contains nickel carbonyl and nickel hydroxide.

Analyses of the substance obtained from toluene gave the following results :

	Calculated for $\text{Ni}(\text{CO})_4 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ .	Found.	
		I.	II.
Carbon .....	11.19	11.66	11.38
Hydrogen .....	2.80	2.95	2.97
Nickel .....	41.26	42.82	42.68

As different samples gave results which differed slightly, it appears that the composition of the substance varies slightly as is apt to be the case in an oxidation product. A precipitate from benzene was found to contain 42.09 per cent. of nickel, while one from chloroform contained 42.81 per cent.

The precipitate carbonizes with sulphuric acid while with dilute acids carbon dioxide is evolved. Sodium or potassium hydroxide attacks the precipitate and apparently removes a portion, since after treatment with one of these alkalies and thoroughly washing, acids will no longer produce effervescence. Potassium iodide is without action; potassium cyanide dissolves it to a brown solution. It is insoluble in chloroform, benzene, toluene, petroleum ether, alcohol, acetone, methyl alcohol, or ether. Ammonium sulphide converts it to the black sulphide of nickel. Although the formula calculated for comparison with the analyses does not account for the evolution of carbon dioxide with an acid, yet this can be explained by the fact that carbon dioxide is invariably a result of the decomposition of nickel carbonyl in solution.

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#### ERRATUM.

In the December issue (1899), on page 1145, in the fourth line of table, for "calcium chloride" read "chloride of lime (bleaching powder)."