Title: ON THE REACTION OF THE NICKEL ION WITH DIMETHYLGLYOXIME

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ON THE REACTION OF THE NICKEL ION WITH DIMETHYLGLYOXIME IN THE PRESENCE OF AN OXIDANT

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/Extract/

Sensitivity of the Reaction

According to a series of published data (1, 2, 4) the sensitivity of the reaction of nickel with H_2Dm /dimethylglyoxime/ increases significantly in the presence of oxidants. Thus Malyuga (1), considers that a tenfold increase in sensitivity takes place.

For an objective evaluation of the sensitivity of the reaction it is convenient to compare the molar coefficients of extinction of the different colored compounds in that region of the spectrum where the maximum absorption of light by the compound concerned is observed.

In Figure 1 are shown the absorption curves of the different products of the interaction of nickel with H_2Dm. Along the abscissa wave lengths are laid out, and along the ordinate the molar coefficients of extinction. The curves were constructed on the basis of measurements with a Pulfrich photometer (with 7 light filters). Curve 1 shows the absorption by the suspended precipitate $Ni(HDm)_2$; curve 2 gives the light absorption of a solution containing the same amount of nickel if the reaction with H_2Dm proceeds in the presence of a solution of iodine when the solution has been alkalized with NH_4OH after all the components have been mixed; finally, curve 3 shows the properties of a solution analogous to the latter, but with NH_4OH replaced by a caustic alkali. It is clear from the curves shown in the Figure that

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the precipitate $Ni(HDm)_2$ is characterized by a maximum in the green portion of the spectrum (when the wave length is about 530 mμ), in which case the molar coefficient of extinction is equal to $\underline{\varepsilon}_1 = 4000$. The absorption of the product formed in the presence of oxidants is shifted to the violet portion of the spectrum, in which case the molar coefficient of extinction is considerably higher, reaching $\underline{\varepsilon}_2 = 12,000$ and $\underline{\varepsilon}_3 = 13,000$. From the Lambert-Beer formula $\lg \frac{I_0}{I} = \underline{\varepsilon} \cdot c \cdot d$, it is evident that equal absorption (for an equal layer thickness d) is obtained under the conditions $\underline{\varepsilon}_1 c_1 = \underline{\varepsilon}_2 c_2$. If it is to be taken into consideration that $\underline{\varepsilon}_1$ is 3 times smaller than $\underline{\varepsilon}_2$, it means that in order to achieve the same light absorption of solutions it is sufficient to take 3 times less nickel in the case when an oxidant is present than for the formation of the usual insoluble compound $Ni(HDm)_2$.

Composition of the Colored Complex

As is known from published data (4), no one has up to this time succeeded in isolating the colored complex formed by the interaction of nickel with H_2Dm in the presence of oxidants. This is explained by the instability of the quadrivalent nickel compound in concentrated solutions and in the solid form. For such cases it is especially expedient to use the method of physico-chemical analysis of solutions of colored complexes (5).

Evidently the real complex is a ternary compound within the system: Ni++ (solution), H_2Dm (solution), oxidant solution. The complete results of the investigation of the corresponding triangular diagram will be given by us separately. A short description of the composition of the complex can be given with the limited data cited below.

For determination of the relation Ni: H_2Dm in the complex (when there is a small excess of the oxidant in NH_4OH) experiments were conducted in the following manner.

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Into a series of test-tubes were introduced the quantities specified
in Table 1 of a 0.01 M acidified solution of nickel sulfate and a 0.01 M
solution of Na_2Dm. Here, in accordance with the condition of physico-
chemical analysis for the determination of composition, the aggregate volume
of these solutions (of equal molarity) remained constant. Then a constant
quantity of 0.01 N iodine solution (in an excess exceeding the quantity of
nickel by several times) was added to all the test-tubes. Next, to each of
the solutions were added 5 mg of concentrated NH_4OH. The solutions were
transferred to the cell (the thickness of the layer was 2 mm) of the Pulfrich
photometer; the extinction measurement was carried out at a wave length of
500 mµ.

It is clear from the results cited in Table 1 that the maximum light
absorption is observed when the relation between the volumes of the nickel
salt and Na_2Dm is equal to 1:2. Thus the proportions in which these com-
ponents react with the formation of the soluble colored complex (in the
presence of a small excess of oxidant) are equal to $Ni^{++}:H_2Dm = 1:2$.

For determination of the ratio of $Ni^{++}:Ox$ (where Ox signifies the
oxidant) a series of experiments were conducted which were analogous to
those preceding in that they maintained the conditions of equal molarity
and equal volumes of the nickel salt and oxidizing solutions. The con-
ditions of the experiments and the results are cited in Table 2; the order
of mixture of the reagents remained strictly the same as was specified above
in the description of the experimental conditions.

The results show that in the formation of the colored soluble complex
nickel and the oxidant react in a proportion of 2:1, for the maximum color-
ation is observed at exactly this ratio.

Thus the basic components of the reaction interact in the following
ratio: $Ni^{++}:H_2Dm : Ox = 1:2:2$. This corresponds to the composition of the
compound isolated by Feigl. However, the problem of the location of the
hydrogen atom has not been solved and, moreover, this complex appears as

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the first, but not the only one in the system. A full study of the composition--behavior diagram for the Ni^{++}, H_2Dm, Ox (in solution) system shows the formation of several compounds. Thus for a ten-fold excess of oxidizer (in relation to nickel) experiments analogous to those described in Table 1 show that in this case the ratio $Ni^{++}:H_2Dm = 1:3$. This compound is formed under the conditions of the qualitative detection of nickel or its colorimetric determination when there is a significant excess of oxidant. When a caustic alkali (instead of NH_4OH) is used, the maximum coloration of the solution is observed near the ratio $Ni^{++}:H_2Dm:Ox = 1:3:3$.

Structure of the Complex

Since the time of Feigl's work it has usually been considered that in the presence of oxidants the complex compound of H_2Dm is formed with quadrivalent nickel, although the ordinary (noncomplex) compounds of the latter are not formed. This view is within the realm of probability, since a considerable number of valency forms of elements in the subgroups are known which are unstable in the form of simple salts and are known only in the form of complexes (for example Mn^{+++}, Co^{+++}, etc.). However, in this case there are still not enough data to permit a conclusion as to what the oxidant reacts with: the nickel ion or the dimethylglyoxime.

The well-known colored $FeCNS^{++}$ complex ion can be obtained through the interaction of Fe^{++}, CNS^-, and Ox in the ratio 1:1:1. However, the knowledge of this relation does not reveal the structure of the complex. It is possible to assume that the oxidant reacts first with the CNS^- ion, oxidizing it to thiocyanogen, and the latter subsequently combines with Fe^{++}. The basis for the usual assumption that $FeCNS^{++}$ is a complex of Fe^{+++} and CNS^- (not of Fe^{++} and CNS) is the existence of the usual Fe^{+++} salts. However, this criterion can not be employed in the case of the complex being studied, since there are no known simple salts of quadrivalent nickel.

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Thus the existence of the intensely colored soluble complex in the Ni^{++}—H_2Dm—Ox system provides equal grounds for two different assertions: 1) it is possible to assume, in agreement with Feigl, that the complex is a combination of H_2Dm with quadrivalent nickel and 2) it could be assumed that the complex is a combination of bivalent nickel with an unstable product of the oxidation of dimethylglyoxime. The following set of data can be cited in favor of the latter conclusion:

1. Dimethylglyoxime in an alkaline solution reacts quite rapidly with various oxidizing agents. Of course the products formed in this case do not generally produce colored compounds with metals. It is possible that when a fixed bond is formed between one oxime group and a nickel ion, the second NOH group can be oxidized with the formation of products (of the nitroso compound type) that are unstable under different conditions and form complexes with metals in this instance.

2. The composition of the compound formed in an alkaline hydroxide solution, as was stated above, approaches the relation Ni^{++}: H_2Dm:Ox = 1:3:3. If it is to be assumed that the oxidant reacts with the nickel, nickel must be accepted here as pentavalent. The assumption that the oxidant reacts with H_2Dm seems more plausible and therefore the relation H_2Dm: Ox remains constant.

3. A comparison of the color intensity of these two solutions was carried out. One contained, in 10 ml of total volume, 1 ml of 0.01 M H_2Dm, an excess of $NiSO_4$, and I_2 (in NH_4OH); and the second, 1 ml of 0.01 M $NiSO_4$, an excess of H_2Dm, and I_2 (also in NH_4OH). The extinction of the first solution was three times smaller than that of the second. This is easily explained if it is assumed that the oxidant reacts with H_2Dm and each bond developing between the Ni^{++} and the oxidized H_2Dm further strengthens the color intensity.

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4. Certain weak oxidizing agents, for example iodine in NaOH (i.e., hypoiodide) and also persulfate in NH_4OH, do not oxidize nickel even to the trivalent state. On the other hand, if dimethylglyoxime is added to a solution of nickel salts in NH_4OH in the presence of $K_2S_2O_8$ or to a suspension of $Ni(OH)_2$ in an alkaline solution of hypoiodide, the solution is colored an intense red.

5. It is known that salts of bivalent iron produce an intense red coloring with H_2Dm in an alkaline solution. If an oxidant (for example H_2O_2) is added to such a solution the red color changes to yellow, whereupon ferric hydroxide cannot be precipitated. On the other hand, a mixture of a salt of trivalent iron and H_2Dm precipitates $Fe(OH)_3$ as a result of the addition of NH_4OH. Thus the Fe^{+++} ion does not form a complex with H_2Dm but, like nickel, forms a stable complex with the unstable product of the oxidation of dimethylglyoxime.

Thus a significant quantity of data points to the conclusion that the generally accepted opinion of Feigl on the structure of the complex under consideration is unfounded. There is a much better foundation for assuming this complex to be a combination of bivalent nickel and an unstable oxidation product of dimethylglyoxime.

Conditions for Use of the Reaction in Detection and Colorimetric Determination of Nickel

1. Order of Mixing of Reacting Substances. In view of the fact that unstable products of interaction take part in the formation of the ternary complex, the correct order of mixing the reagents is of very essential importance. On the basis of the data cited above, the following step-by-step methods can be considered for conducting the reaction in an alkaline solution: a) The dimethylglyoxime is added last (i.e., the order of mixing is as follows: NH_4OH, Ni^{++}, Ox, H_2Dm). This method gives satisfactory

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results only when weak oxidizing agents are used. In the case of strong oxidants $Ni(OH)_3$, which reacts slowly with H_2Dm, is precipitated, while an excess of the oxidant breaks down the H_2Dm. b) The oxidant is added last (i.e., the order is as follows: NH_4OH, Ni^{++}, H_2Dm, Ox). In this case there is first formed the precipitate $Ni(HDm)_2$, which reacts very slowly with the oxidant, and therefore the reaction proceeds unsatisfactorily. c) The nickel salt is added last. This method gives unsatisfactory results, since the oxidant breaks down the dimethylglyoxime before the latter can interact with the nickel. d) The best method for formation of the complex consists of mixing Ni^{++}, H_2Dm, and Ox in an acid solution (when there is no interaction), after which the alkali is quickly added to the mixture.

2. _Proportion of the Reagents._ Detailed experiments on the ternary system of Ni^{++} -H_2Dm-Ox show that all isochromes (lines of identical color) are shifted to the side opposite to ⋀the region corresponding to excesses of dimethylglyoxime. This is connected with the fact that when there is an excess of H_2Dm the latter becomes strongly bound to nickel in the forms of the insoluble (and weakly colored) $Ni(HDm)_2$ complex. Therefore the solution must contain an excess of oxidant in comparison with dimethylglyoxime. Thus the proportion of reacting substances must correspond to the condition:

$$(Ox) > (H_2Dm) > 3(Ni^{++}).$$

3. _Selection of the Oxidant._ All the characteristics of the reaction stated above indicate that the use of extremely strong oxidant in large excess can lead to unfavorable results. In literature there is an indication (1) that an excess of bromine leads to a diminished effect. This is doubtlessly connected with the breaking down of H_2Dm by an excess of a strong oxidant. Therefore iodine, proposed by D. P. Malyuga (2), seems to be one of the most suitable oxidants, especially in the presence of NH_4OH (Note: It is true that when there are excessive quantities of iodine, nitrogen iodide may be formed). The use of a caustic alkali in place of NH_4OH intensifies the color somewhat, but causes a weakening of it on long standing.

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Conclusions

The reaction of nickel with dimethylglyoxime in the presence of oxidizing agents has been studied. It has been shown that the molar coefficient of extinction is a convenient characteristic for determining the relative sensitivity of the reaction; by this method it was found that the sensitivity of the reaction of nickel with dimethylglyoxime increases 3 times in the presence of oxidants.

The composition of the complex was studied with the help of the method of the physico-chemical analysis of solutions. It was found that when there is a small excess of oxidant, the composition of the complex corresponds to a relation of nickel to dimethylglyoxime equal to 1:2. When there is a large excess of oxidant this relation equals 1:3.

The structure of the complex has been discussed. Evidence has been cited to the effect that, contrary to Feigl's opinion, the complex is a combination of Ni^{++} and an unstable product of the oxidation of dimethylglyoxime.

On the basis of data on the composition and structure of the complex, a rational foundation was established for determining conditions under which the reaction should be conducted.

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Editorial: Please reproduce 2 tables and 1 drawing from attached sheet.

Table 1

Light Absorption Test for Nickel : Dimethylglyoxime Ratio

0.01-M I_2 in ml	0.01-M $NiSO_4$ in ml	0.01-M Na_2Dm in ml	Ratio Ni^{++} : H_2Dm	Extinction lg $\frac{I_0}{I}$
6	0.8	3.2	1 : 4	0.75
6	1.0	3.0	1 : 3	0.97
6	1.33	2.67	1 : 2	1.05
6	2.0	2.0	1 : 1	1.00
6	2.67	1.33	1 : 0.5	0.62

Table 2

Light Absorption Test for Nickel : Oxidizer Ratio

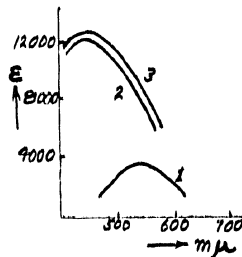| 0.01-M Na_2Dm in ml	0.01-M $NaSO_4$ in ml	0.01 N I_2 in ml	Ratio Ni : Ox	Extinction lg $\frac{I_0}{I}$
5	1.00	4.00	1 : 4	0.47
5	1.25	3.75	1 : 3	0.88
5	1.67	3.35	1 : 2	0.95
5	2.50	2.50	1 : 1	0.90
5	3.34	1.66	1 : 0.5	0.66

Figure 1. Extinction Curves of Dimethylglyoxime Nickel [Ni (HDm)₂ and oxidized complex]

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