THE REACTION OF HYDROXYLAMINE
WITH TETRACYANONICKELATE(II) IN AN INERT ATMOSPHERE

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The reaction of hydroxylamine with tetracyanonickelate(II) in an inert atmosphere gives rise to nitrogen and ammonia, tricyanonitrosonickelate being a reaction intermediate. The appearance of this intermediate cannot be ascribed to an intermediary formation of nitroxyl. The reactive intermediate seems to be tricyanohydroxylaminenickelous ion. Nitrogen is produced by the reaction of tricyanonitrosonickelate with hydroxylamine. The reaction is catalysed by traces of certain metallic ions and inhibited by cyanides.

The reaction of hydroxylamine with tetracyanonickelate(II) in an alkaline medium yields the intensely coloured tricyanonitrosonickelate[1-4]. Hieber and coworkers[1,2] interpret its formation as due to disproportionation of hydroxylamine to nitroxyl (HNO) and ammonia, followed by substitution of the nitroxyl anion (NO^-) for a CN^- anion in tetracyanonickelate.

We have demonstrated[5] that the course of the reaction of hydroxylamine with tetracyanonickelate depends on whether it is conducted under an inert atmosphere or in the presence of oxygen. We have also shown[5] that in the presence of oxygen the intermediary nitroxyl cannot be postulated. The present paper deals with the reaction of hydroxylamine with tetracyanonickelate(II) in an inert atmosphere.

EXPERIMENTAL

Chemicals. All the chemicals employed were of A.R. purity. Hydroxylamine hydrochloride and potassium tetracyanonickelate (prepared according to[6]) were twice recrystallized prior to use.

Apparatus and procedure. The concentration of tricyanonitrosonickelate in relation to time was followed spectrophotometrically. The reaction proceeded in a thermostated vessel, connected with a through-flow cell of the spectrophotometer. The apparatus is described in detail in a recent paper[7]. The reaction mixture was bubbled with nitrogen that had been brought to the temperature of the reaction mixture by passage through a thermostated solution of the same composition as that of the reaction mixture except that hydroxylamine was absent. The nitrogen had been freed from traces of oxygen by washing in solutions containing a chromium (II) salt and a zinc amalgam. The concentration of tricyanonitrosonickelate was followed by measuring the absorbance of the solution at 498 nm with a Spekol spectrophotometer (Carl Zeiss, Jena), connected to a recorder EZ 2 (Laboratorní přístroje, Prague). The concentration of tricyano-nitrosonickelate was calculated from the molar absorptivity[5] 427 mol^{-1} 1 cm^{-1}.

In measuring the formation rates of ammonia and nitrogen the reaction proceeded in the thermostated vessel. In experiments designed to measure the formation rate of ammonia the latter was displaced from the solution by nitrogen, absorbed in sulphuric acid and determined at selected time intervals titrimetrically or colorimetrically after neutralisation. The formation rate of nitrogen was measured with the aid of a thermostated gas burette. In the gaseous products nitrogen and dinitrogen monoxide were determined at time intervals with a chromatograph Chrom 3 (Laboratorní přístroje, Prague). After the removal of ammonia the gaseous mixture was dried by passage through a column packed with pellets of KOH. A satisfactory separation of nitrogen and dinitrogen monoxide was achieved at 125°C with hydrogen as carrier in a column 2 400 mm long packed with activated carbon. The linear dependence of the heights of peaks on concentrations of the two gases (for samples not exceeding 500 μl at 20°C) was verified by calibration.

The concentrations of hydroxylamine in the stock solutions were checked by determining hydroxylamine according to Bhaskara-Rao[8].

RESULTS AND DISCUSSION

Stoichiometry of the Reaction

Unlike the reaction proceeding in the presence of oxygen, the reaction of hydroxylamine with tetracyanonickelate(II) in an inert atmosphere is much slower and gives rise to ammonia. At room temperature the amount of tricyanonitrosonickelate formed in the reaction mixture ($2 \cdot 5$M-KOH, $0 \cdot 05$M-K$_2$[Ni(CN)$_4$], $0 \cdot 1$M-NH$_2$OH) was not measurable even after 4 h. After elevation of the reaction temperature to 50°C the violet coloration of tricyanonitrosonickelate appeared immediately on mixing the reaction components and the nitrogen passed through the solution contained ammonia. When the inert atmosphere was replaced by oxygen tricyanonitrosonickelate was formed on mixing the reaction components even at room temperature but ammonia was not detected even on raising the temperature to 70°C.

To determine the stoichiometry of the reaction in an inert atmosphere, tricyanonitrosonickelate and ammonia were determined simultaneously at different stages of the reaction. The amount of ammonia was always greater than would correspond to Hieber's molar ratio $NH_3 : [Ni(CN)_3NO]^{2-} = 1 : 1$.

In view of the previously propounded mechanism of the reaction of hydroxylamine with tetracyanonickelate, and the postulated intermediary nitroxyl, nitrogen and dinitrogen monoxide should be present among the reaction products. For this reason we determined the composition of the gaseous mixture formed under various conditions either by decomposition of an alkaline solution of hydroxylamine or by reaction of hydroxylamine with tetracyanonickelate. It appeared that decomposition of the alkaline solution of hydroxylamine always gave a mixture of ammonia, nitrogen and dinitrogen monoxide, the molar ratio of nitrogen and dinitrogen monoxide being (3 to 5): 1. By contrast, decomposition of the alkaline solution of hydroxylamine in the presence of tetracyanonickelate yielded only ammonia and nitrogen (not even a trace of dinitrogen monoxide was detected.)

The Kinetics

Experiments shoved that the reaction of hydroxylamine with tetracyanonickelate cannot be described by a simple kinetic equation. Therefore, we first investigated the initial formation rate of tricyanonitrosonickelate in relation to concentrations of the reactants. The starting concentration of hydroxylamine was varied in the range from 0·0003 to 1M at $[Ni(CN)_4^{2-}] = 5 . 10^{-2}$M, $[OH^-] = 2$M and $t = 50°C$; the starting concentration of potassium tetracyanonickelate from 0·0001 to 0·03M at $[NH_2OH]_0 = 0·05$M, $[OH^-] = 2$M and $t = 50°C$. It appeared that in the concentration range of hydroxylamine and tetracyanonickelate from 10^{-4}M to 10^{-2}M the initial formation rate of tricyanonitrosonickelate was approximately constant, $v_0 \doteq 5 . 10^{-8}$ mol . $.1^{-1} s^{-1}$. At higher concentrations of hydroxylamine $(>0·1$M$)$ the initial rate increased with increasing concentration of hydroxylamine, $v_0 \doteq k[NH_2OH]_0$. The dependence of the initial rate on the concentration of tetracyanonickelate was not investigated beyond the limit $[Ni(CN)_4^{2-}]_0 = 0·03$M, since at higher concentrations the results would he distorted by the absorbance of tetracyanonickelate itself.

Like the reaction of hydroxylamine with tetracyanonickelate in an oxygen atmosphere, the reaction in the inert atmosphere was catalysed by traces of some ions. The order of the catalytic effects of metallic ions was $Cu(II) > Ni(II) > Fe(II) > Co(II)$, the effect of cobaltous ions being practically zero. A marked inhibitory effect was observed with cyanide only. We investigated in more detail the effects of additions of nickelous and cyanide ions, *i.e.* the effect of composition of the cyano-
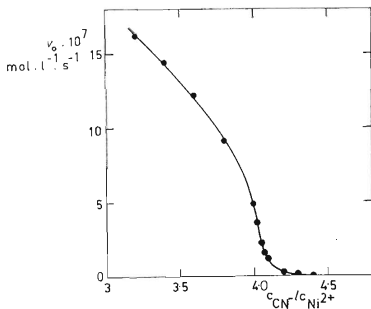

Fig. 1

The Initial Formation Rate of $[Ni(CN)_3NO]^{2-}$ as a Function of $c_{CN^-}/c_{Ni^{2+}}$

The different ratios $c_{CN^-}/c_{Ni^{2+}}$ were achieved by additions to a 10^{-2}M solution of $K_2[Ni.(CN)_4]$, $[NH_3OH]_2 = 0·8$M, $[OH^-] = 1$M, 50°C.

nickelous complex on the initial formation rate of tricyanonitrosonickelate. As can be seen from Fig. 1, the reaction rate decreased with the increasing ratio $c_{CN^-}/c_{Ni^{2+}}$. When this ratio exceeded the value of 4·3 the reaction practically stopped.

With increasing alkalinity of the solution the initial reaction rate increased. In the range $[OH^-] = 1$ to $3M$ the dependence of the initial rate on concentration of hydroxyl ions was approximately linear. At $[OH^-] > 3M$ the values of v_0 were lower than would correspond to a linear relation. The deviations were probably caused by hydroxocyanonickelous complexes, known to be formed in alkaline media.

Further we have followed the kinetics of the formation of tricyanonitrosonickelate at different concentration ratios of the reactants. Fig. 2 shows the time dependence of concentration of tricyanonitrosonickelate at different ratios $[Ni(CN)_4^{2-}]$: : $[NH_2OH]_0$.

If $[Ni(CN)_4^{2-}] \geqq [NH_2OH]_0$ the reaction rate kept constant in a long period and the reaction appeared to be of zero order with respect to both tetracyanonickelate and hydroxylamine. If $[NH_2OH]_0 > [Ni(CN)_4^{2-}]_0$ the initial reaction rate increased with increasing concentration of hydroxylamine, but the degree of conversion attained in 10 h was lower. If $[NH_2OH]_0 \gg [Ni(CN)_4^{2-}]_0$ the concentration of tricyanonitrosonickelate reached a final constant value after a certain time, but the
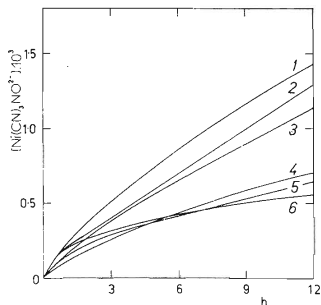

FIG. 2

Concentration of Tricyanonitrosonickelate as a Function of Time at Different Ratios $[Ni(CN)_4^{2-}]_0/[NH_2OH]_0$

$[OH^-] = 1M$, 50°C; *1—3*: $[NH_2OH]_0 =$ = 0·0052M, *4—6*: $[Ni(CN)_4^{2-}]_0 = 0·0025M$, $[Ni(CN)_4^{2-}]_0/[NH_2OH]_0$: *1* 4·8, *2* 2·4, *3* 1·44, *4* 0·2, *5* 0·1, *6* 0·003.
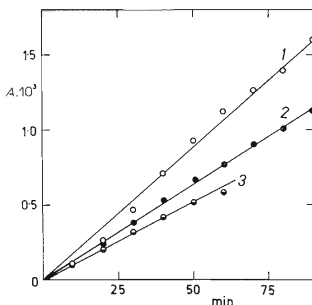
FIG. 3

Mechanism I. The dependence of $A = -a.\ln$. $(a - x)/a - x$ on t

$a = [Ni(CN)_4^{2-}]_0$; $x = [Ni(CN)_3NO^{2-}]$; $[Ni(CN)_4^{2-}]_0 = 0·006M$; $[NH_2OH]_0 = 0·6M$; 50°C; *1* $[OH^-] = 6M$; *2* $[OH^-] = 5M$; *3* $[OH^-] = 4M$.

concentration of hydroxylamine kept decreasing with time, ammonia and nitrogen being formed.

We also investigated the time course of the formation of ammonia and nitrogen at $[NH_2OH]_0 \gg [Ni(CN)_4^{2-}]_0$ (the concentrations were 3M and 0.02M, respectively). For the reaction to be sufficiently fast it was conducted at a rather high temperature (96°C) in a strongly alkaline medium (5M-KOH). The concentration of tricyano-nitrosonickelate attained a constant value in a few minutes. It was established that if $d[Ni(CN)_4^{2-}]/dt = 0$, then

$$d[NH_3]/dt = d[N_2]/dt = k''.[NH_2OH].\qquad(1)$$

The validity of equation (1) was demonstrated up to an 80% conversion degree of hydroxylamine for the formation rates of both ammonia and nitrogen. The value of k'' for the given reaction mixture was $1.35 . 10^{-5} \text{ s}^{-1}$. In view of the great excess of hydroxylamine the reaction was rather decomposition of an alkaline solution of hydroxylamine than its reaction with tetracyanonickelate. Nevertheless, decompositions of hydroxylamine in an alkaline solution with and without tetracyano-nickelate took different courses. In the former case only ammonia and nitrogen were formed, in the latter there were formed ammonia, nitrogen and dinitrogen monoxide.

Mechanism of the Reaction

The reported mechanism[1,2] of the reaction of hydroxylamine with tetracyanonickelate starts from the idea that the only reaction products are tricyanonitrosonickelate and ammonia. This paper, however, demonstrates that the actual products are nitrogen and ammonia, tricyanonitrosonickelate being an intermediate. Hieber and coworkers[1,2] explain the formation of tricyanonitrosonickelate by dismutation of hydroxylamine to ammonia and nitroxyl, followed by a reaction of nitroxyl with tetracyanonickelate. This mechanism, however, is at variance with some results described in the present paper:

a) The conception of the intermediary nitroxyl is not compatible with equation (1), valid on attaining a steady state $(d[Ni(CN)_4^{2-}]/dt = 0)$.

b) If the formation of tricyanonitrosonickelate were governed by dismutation of hydroxylamine, giving rise to nitroxyl, the dependence of the formation rate of tricyanonitrosonickelate on concentration of the reactants (Fig. 2) could not be explained.

c) The reaction products did not contain even a trace of dinitrogen monoxide, which would be expected as arising from dimerization of nitroxyl. This fact cannot be explained by the assumption that the formed nitroxyl reacts with tetracyanonickelate before it can dimerize, because no dinitrogen monoxide is formed even by complete

decomposition of a 150-fold excess of hydroxylamine with respect to tetracyano-nickelate.
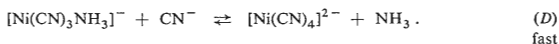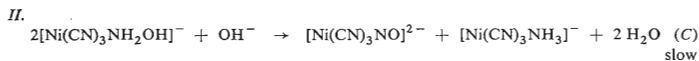
An acceptable interpretation of the reaction course seems to be the idea that the intermediate is a complex formed by replacement of a cyanide group in tetracyano-nickelate by a molecule of hydroxylamine. According to this idea, also employed to interpret the reaction of hydroxylamine with tetracyanonickelate in an oxygen atmosphere[5], the reaction in an inert atmosphere can be described by two reaction schemes. Either is based on the assumption of a rapid equilibrious substitution of hydroxylamine for a cyanide group in tetracyanonickelate:

$$[Ni(CN)_4]^{2-} + NH_2OH \;\rightleftharpoons\; [Ni(CN)_3NH_2OH]^- + CN^- . \qquad (A)$$
$$\text{fast}$$
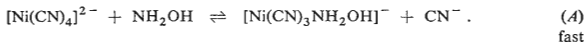
According to the first reaction scheme (I) reaction (A) is followed by reaction of the tricyanohydroxylaminenickelous complex with another molecule of hydroxylamine:

I.

$$[Ni(CN)_3NH_2OH]^- + NH_2OH + OH^- \;\rightarrow\; [Ni(CN)_3NO]^{2-} + NH_3 + 2\,H_2O . \quad (B)$$
$$\text{slow}$$
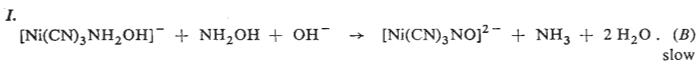
According to the second reaction scheme (II) the tricyanohydroxylaminenickelous complex dismutes and the arising tricyanoaminenickelate reacts with cyanide to tetra-cyanonickelate

II.

$$2[Ni(CN)_3NH_2OH]^- + OH^- \;\rightarrow\; [Ni(CN)_3NO]^{2-} + [Ni(CN)_3NH_3]^- + 2\,H_2O \quad (C)$$
$$\text{slow}$$

$$[Ni(CN)_3NH_3]^- + CN^- \;\rightleftharpoons\; [Ni(CN)_4]^{2-} + NH_3 . \qquad (D)$$
$$\text{fast}$$

The equilibrium of the last reaction is shifted strongly to the right side, since the ultraviolet absorption spectrum of tetracyanonickelate was not changed even at a 10^4 excess of ammonia.

Tricyanonitrosonickelate (arising according to scheme I or II) reacts with hydroxylamine:

$$[Ni(CN)_3NO]^{2-} + NH_2OH + CN^- \;\rightarrow\; [Ni(CN)_4]^{2-} + N_2 + H_2O + OH^- . \ (E)$$
$$\text{slow}$$
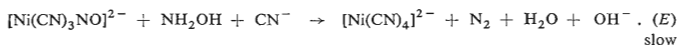
The kinetic evaluation of the two variants leads to a differential equation. However, it is only after introduction of simplifying assumptions that its integration yields a function relating the concentration of tricyanonitrosonickelate to the concentrations of the reactants. If the starting concentrations of the reactants are designated

$[\text{Ni(CN)}_4^{2-}]_0 = a$, $[\text{NH}_2\text{OH}]_0 = b$, $[\text{Ni(CN)}_3\text{NO}^{2-}] = x$, concentration of the intermediate $[\text{Ni(CN)}_3\text{NH}_2\text{OH}^-] = y$ and concentration of the product $[\text{N}_2] = z$, and provided that $x \gg y$, $x \gg z$, $b \gg a$ it holds for the first reaction scheme (reactions (A), (B) and (E)):

$$\mathrm{d}x/\mathrm{d}t = k \cdot K_1 \cdot b^2 (a - x)/x, \qquad (2)$$

where k is the rate constant of reaction (B), $K_1 = y \cdot x/(a - x) \cdot b$ the equilibrium constant of reaction (A). Integration of equation (2) yields after rearrangement:

$$k \cdot K_1 \cdot b^2 \cdot t = -x - a \cdot \ln(a - x)/a \qquad (3)$$

In Fig. 3 is plotted the right-hand side of equation (3) vs time for the measured concentrations of tricyanonitrosonickelate.

Under the same assumptions it holds for the second reaction scheme (reactions (A), (C), (D), (E)).

$$\mathrm{d}x/\mathrm{d}t = k'' \cdot K_1^2 \cdot b^2 \cdot (a - x)^2/x^2, \qquad (4)$$

where k'' is the rate constant of reaction (C). Integration of equation (4) gives after rearrangement:

$$k'' \cdot K_1^2 \cdot b^2 \cdot t = 2a \cdot \ln(a - x)/a + a^2/(a - x) - (a - x). \qquad (5)$$

The right-hand side of equation (5) is plotted vs time for the measured concentrations of tricyanonitrosonickelate in Fig. 4. Figs 3 and 4 show that the reaction is described better by equation (3), based on Scheme I, according to which the formation of tri-
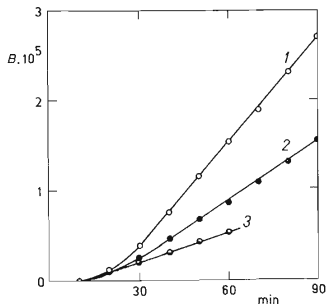

FIG. 4

Mechanism *II*; The Dependence of $B = 2a \cdot \ln(a - x/a) + (a^2/a - x) - (a - x)$ on t
$a = [\text{Ni(CN)}_4^{2-}]_0$; $x = [\text{Ni(CN)}_3\text{NO}^{2-}]$; $[\text{Ni(CN)}_4^{2-}]_0 = 0.006\text{M}$; $[\text{NH}_2\text{OH}]_0 = 0.6\text{M}$; 50°C; *1* $[\text{OH}^-] = 6\text{M}$; *2* $[\text{OH}^-] = 5\text{M}$; *3* $[\text{OH}^-] = 4\text{M}$.

cyanonitrosonickelate is controlled by the reaction of hydroxylamine with tricyano-hydroxylaminenickelate. Under assumptions analogous to those employed with the reaction Schemes *I* and *II*, we also kinetically processed the conception that an inter-mediate in the formation of tricyanonitrosonickelate was a dicyanodihydroxyl-aminenickelous complex in equilibrium with tetracyanonickelate and hydroxylamine. However, this idea has failed to lead to an expression describing the actual reaction course.

As has been shown, at $[NH_2OH]_0 \gg [Ni(CN)_4^{2-}]_0$, a high temperature and alka-linity the system tetracyanonickelate–hydroxylamine attains a steady state, which can be characterized by $d[Ni(CN_3)NO^{2-}]/dt = d[Ni(CN)_3NH_2OH^-]/dt = d[Ni(CN)_4^{2-}]/dt = d[CN^-]/dt = 0$.

Under this condition the formation rate of nitrogen (ammonia) is linearly pro-portional to the concentration of hydroxylamine (equation (*1*)). This fact and the observation that decomposition of hydroxylamine in the presence of tetracyano-nickelate produces no dinitrogen monoxide or hyponitrite, but only nitrogen, de-monstrate the existence of the subsequent reaction of hydroxylamine with tricyano-nitrosonickelate. This reaction has not been reported yet, but an analogous reaction of the nitroprusside complex with hydroxylamine is well known[9].

A more detailed kinetic study of the overall and the individual reactions meets with difficulties. To render the reaction sufficiently fast the alkalinity and temperature of the medium must be high. These conditions produce the formation of a mixture of hydroxocyanohydroxylaminenickelous complexes, which makes the results dif-ficult to interpret. (At $[OH^-] > 8M$ a blackish brown precipitate separates from solutions of tetracyanonickelate; on dilution it dissolves). What also makes the kinetic study difficult is the impossibility of concentration determinations of hydroxylamine, tricyanonitrosonickelate, nitrogen and ammonia for a common point of time, especially at the early stage of the reaction.

REFERENCES

1. Hieber W., Nast R., Proeschel E.: Z. Anorg. Allgem. Chem. *256*, 145 (1948).
2. Hieber W., Nast R., Proeschel E.: Z. Anorg. Allgem. Chem. *256*, 156 (1948).
3. Hughes M. N., Nicklin H. G.: Chem. Ind. (London) *1967*, 2176.
4. Hughes M. N., Nicklin H. G.: J. Chem. Soc. A *1971*, 164.
5. Vepřek-Šiška J., Luňák S.: This Journal *37*, 3846 (1972).
6. *Inorganic Synthesis* II., p. 227, W. C. Fernelius, McGraw Hill, New York 1946.
7. Vepřek-Šiška J., Mádlo K., Hasnedl A.: This Journal *36*, 3096 (1971).
8. Bhaskara-Rao K.: Chemist Analyst *49*, 40 (1960).
9. Hofmann K. A.: Ann. Chem. *312*, 1 (1900).