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A Survey of the Reaction of the Coordinated Nitrite Ions of the Nitro-Ammine-Co (III) Complexes.*,**

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Both the reduction and the oxidation of the nitrite of the nitro-ammine-cobalt(III) complexes are much slower than that of the free nitrite. In general there is a parallelism between the rate of aquation of the complex and the rate of the redox reaction of the coordinated nitrite. In oxidation reactions there is no detectable intermediate. Oxidizing the mononitro complex the original valence state of the central cobalt(III) ion is preserved, with other complexes a gradual reduction of the central ion occurs. In reduction reactions more or less stable intermediates can be detected. With azide ion the intermediate is not identical with that of the reaction of the azidopenta-amminecobalt(III) complex with nitrite. The coordinated ligands act on the reactivity of a particular ligand either through their effect on the electron distribution of the whole complex or by means of a direct chemical interaction between adjacent ligands.

Introduction

The effect of coordination on the rate and the mechanism of the redox reactions of the various ligands is obviously a very important, but a surprisingly scantly studied problem. In connection with investigations of the catalytic properties of complexes[1] we began a systematic study of this problem. Nitrite ion was chosen as a reactive ligand and cobalt(III) as a central ion. In our opinion the nitro-ammine-Co(III) complexes are almost ideally suited for such a study. Namely this ligand can be both reduced and oxidized, the whole series of the successive complexes is known and well defined, there is a possibility to study the effect of the foreign ligands and of the steric arrangements in the coordination sphere, of the charge of the complexes and of the linkage isomerism. The complexes are inert, so the disturbing action of the reactions of the uncoordinated ligand does not occur. However, it must be borne in mind that the higher complexes of the series $Co(NH_3)_{6-n}(NO_2)_n^{3-n}$ decompose relatively rapidly, especially at lower pH.

Dealing with the effect of the coordination on the reactions of a substance, the following immediate questions have to be answered :

1. How does the coordination influence the rate of the reaction?

2. Which species are formed as more or less stable intermediates and what is the relation between these intermediates and those of the reactions with the free ligand?

3. What is the effect of the other ligands and the steric arrangements of the coordination sphere on the rate and the mechanism?

Several other questions may be arise,but at the present state of affairs we have to be content with answers on the aforementioned questions. It is not easy to answer satisfactorily even the very first question. Namely, we are lacking the basic data for the comparison, because there is no satisfying kinetic study of the reactions between nitrite and different oxidants, and between nitrite and iodide. Another difficulty in the comparison is the inherent complexity of the reactions of complexes containing more than one nitro group. Initially the number of parallel reactions is evidently equal with the number of nitrite ions in the coordination sphere. The situation becomes even more complicated in the next stage of the reaction, when the further reactions of each product of the initial reactions also occur. It is evident, that the only comparable measure of the reactivity of the ligands in these cases is the initial rate. Nevertheless, the study of the higher complexes may provide interesting and important qualitative information.

Experimental Section

Materials. In all experiments c.p. reagents were used. The following complexes were prepared according to standard methods: mononitropentaammine-cobalt(III) complex (as chloride salt)[2], *cis*-dinitrotetra-amminecobalt(III) (as sulphate)[3], *trans*-dinitrotetra-amminecobalt(III) (as chloride)[4], *cis-trans*-trinitro-triamminecobalt(III)[5], *trans*-diamminetetranitro-cobalt(III) (as ammonium salt)[6], amminepentanitro-cobalt(III) (as potassium salt)[7], *cis*-chloronitrobis(ethylenediamine)cobalt(III) (as chloride)[8], *trans*-chloronitrotrobis(ethylenediamine)cobalt(III) (as ni-

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(**) Part II. of the series: Reactions of the Coordinated Substances. Part. I.: M. T. Beck and O. Kling, *Acta Chem. Scand.*, *15*, 453 (1961).

(1) M. T. Beck, *Record of Chemical Progress*, *27*, 37 (1966).

(2) S. M. Jörgensen, *Z. anorg. Chem.*, *5*, 169 (1894).

(3) S. M. Jörgensen, *Z. anorg. Chem.*, *11*, 430 (1896).

(4) S. M. Jörgensen, *Z. anorg. Chem.*, *17*, 469 (1898).

(5) S. M. Jörgensen, *Z. anorg. Chem.*, *7*, 310 (1894).

(6) S. M. Jörgensen, *Z. anorg. Chem.*, *17*, 477 (1898).

(7) Y. Shibata, *Inorg. Chem.*, *3*, 11 (1964).

(8) A. Werner, *Berichte*, *34*, 1734 (1901).

trate)[8], and red nitrosylpentaamminecobalt(III) (as nitrate)[9].

Kinetic experiments were performed by measuring the change of absorbancy during the reactions using a Beckman B spectrophotometer.

All of the reactions were studied in the dark at room temperature (22 ± 1°C) without thermostat control. In case of the reaction with iodide even the traces of oxygen interfered, so these experiments were performed in nitrogen atmosphere in an all glass apparatus. The nitrogen was freed from oxygen using a solution of pentacyanocobalt(II) complex. In case of diazotation/coupling reaction the amine and the coupling agent were added simultaneously unless otherwise noted in the text.

Determination of nitric oxide was made for of reactions with iodide. The carrier gas (nitrogen) was bubbled through a solution of containing Fe(II)/15 g $(NH_4)_2Fe(SO_4)_2 . 12H_2O + 70$ ml water $+ 5$ ml concentrated H_2SO_4/, the absorbancy of which was continuously measured at 450 mm.

Results and Discussion

Oxidation reactions. Oxidations with permanganate and cerium(IV) nitrate were studied. Absorbancy *versus* time curves are shown on Fig. 1. The dramatic decrease of the reaction rate in case of both oxidants is striking. The oxidation with permanganate exhibits two remarkable features. First, there is a decrease of the reaction in time, though in general the permanganate oxidations are typical autocatalytic reactions. This autocatalytic nature of reaction was also observed[10] in case of the oxidation of ethylenediaminetetraacetatochromium(III) complex. Secondly, after a certain reaction time the absorbancy increases again, due to the formation of MnO_2 precipitate. MnO_2 formation does not occur at the same acidity with free nitrite, however its formation could be observed in case of oxidation of ethylenediaminetetraacetic acid coordinated to chromium(III). The order of the initial rates is the same with permanganate and cerium(IV) nitrate:

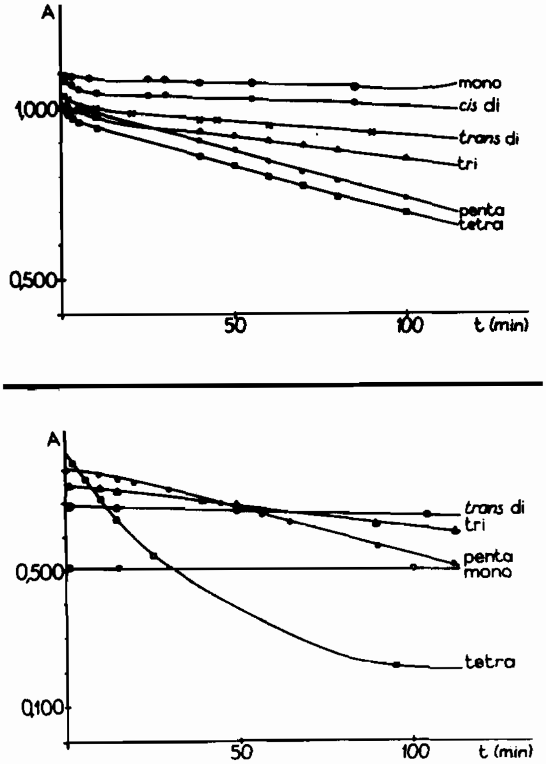

Figure 1. Oxidation of complexes with MnO_4^- and Ce^{4+}, resp. Composition of reaction mixtures in case of permanganate oxidation : $C_{KMnO_4} = 4{,}76.10^{-4}$M ; $C_{coord.NO_2^-} = 1{,}19.10^{-3}$M ; $C_{HClO_4} = 0{,}12$ M. Wavelength 530 mμ, cell 1 cm. Composition of reaction mixtures in case of cerium(IV) oxidation : $C_{(NH_4)_2Ce(NO_3)_6} = 4{,}5.10^{-3}$M; $C_{coord.NO_2^-} = 1{,}13.10^{-3}$M; $C_{HNO_3} = 1$M. Wavelength 410 mμ, cell 1 cm.

Reaction with MnO_4^-: *cis*-di $\sim$ mono $<$ *trans*-di $<$ tri $<$ penta $<$ tetra $<$ hexa $\lll$ NO_2^-.

The oxidation of the *cis*-dinitrotetraamminecobalt(III) with cerium(IV) could not be studied because the solutions became turbid at mixing. This phenomenon may indicate a specific interaction between the complex and cerium(IV), but it has not been studied further.

In case of oxidation reactions there is no detectable intermediate. The nitrate ion formed in the reaction is easily substituted by a molecule of water. The most important problem of these reactions is the fate of the central ion during the reaction. We found that in case of the mononitro complex both electrons are transferred to the oxidant, and the complex is practically quantitatively transformed into the aquopentaamminecobalt(II). Increasing the number of nitro groups in the complex there is an increasing tendecy toward the partial reduction of the central cobalt(II) ion, and if the number of nitro groups exceeds three, the reduction of the central ion is complete. The mechanism of the oxidation of the mononitropentaamminecobalt(III) complex with cerium(IV) is schematically shown on Fig. 2.

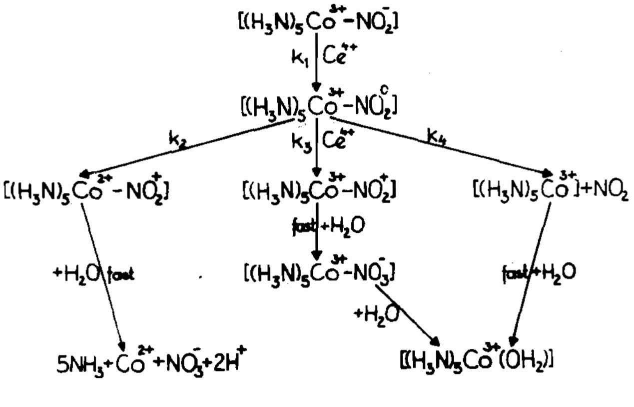

Figure 2. Scheme of the oxidation of the coordinated nitrite. In case of mononitropentaamminecobalt(III) complex $k_3, k_4 \gg k_2$, that it is no reduction of central cobalt(III) occurs, in case of dinitrotetraamminecobalt(III) complex $k_3, k_4 \sim k_2$, that is the reduction of cobalt(III) center is partial, while with complexes containing more than two nitro groups $k_2 \gg k_3, k_4$, that is the reduction of central ion is practically complete.

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(9) A. Werner and P. Karrer, *Helv. Chim. Acta*, *1*, 54 (1919).

(10) M. T. Beck and O. Kling, *Acta Chem. Scand.*, *15*, 453 (1961).

The decrease of the reactivity of the coordinated nitrite can be explained considering that on the effect of coordination the electrons of the ligand are shifted toward the central ion. The decrease of the electron density evidently results in the decrease of the probability of the bond formation with an electrophile reagent, so the diminution of the rate of the oxidation is easily understandable. Comparing the initial rates a parallelism between the rate of aquation and that of the oxidation of the coordinated nitrite ion can be observed. The same trans effect exists in these oxidation reactions as in case of aquations. This finding was corroborated by comparing the behaviour of the *cis*- and *trans*-chloronitrobis(ethylenediamine) cobalt(III) complexes. The rate order was

$$\text{trans} > \text{mono} > \text{cis}.$$

Reduction reactions. In the reduction reactions the following rate orders were foud :

Reaction with I^-: $\textit{cis}\text{-di} < \text{mono} < \text{tri} \sim \text{penta} < \textit{trans}\text{-di} < \text{tetra} < \text{hexa} \ll NO_2^-$;

Reaction with N_3^-: $\textit{cis}\text{-di} < \text{mono} < \text{tri} < \text{penta} \sim \textit{trans}\text{-di} < \text{tetra} < \text{hexa} \ll NO_2^-$;

Reaction with sulphanilic acid and α-naphtylamine : $\text{mono} < \textit{trans}\text{-di} < \textit{cis}\text{-di} < \text{tri} < \text{penta} < \text{tetra} < \text{hexa} \ll NO_2^-$.

It appears that the coordination results in the decrease of the reactivity in case of the reduction of the nitrite just as in case of oxidation reactions. In interpreting this finding one must consider that the coordination decreases the proton affinity of the nitrite ion. In the reduction of nitrite ion, it is always assumed that the first step is the protonation which is followed by the loss of a molecule of water, leading to the formation of NO^+, which is considered to be the reactive species. The observed diminution of the rate of the reduction reactions can be explained by the hindrance of protonation of the coordinated nitrite ion. Before interpreting the different rate orders some characteristics of each of the reactions have to be discussed.

Reaction with iodide. It appeared that with the first three members of the successive complexes, i.e. with the mononitro, dinitro and trinitro complexes, the reduction of the cobalt(III) center is much slower than the reduction of the coordinated nitro groups. Therefore only these complexes and the *cis* and *trans* cloronitrobis(ethylenediamine)cobalt(III) complexes were studied in detail. It was foud that the amount of iodine formed is much less than stoichiometric. It was further observed that the amount of nitric oxide released is also much smaller than would be expected on the basis of a quantitative reaction. The spectrum of the product (Fig. 3) which was recorder after adding a small excess of thiosulphate to eliminate the iodine, clearly indicates that it is not the aquopentaamminecobalt(III) complex. It is not identical with the «red nitrosylpentaamminecobalt(III)» complex either, the structure of which is not definitely known.[11,12] Our product is most probably the nitrosopentaaminecobalt(III) complex containing a neutral NO ligand, while the «red complex» is either a dimer, or a nitroso complex containing a negatively charged NO^- ligand

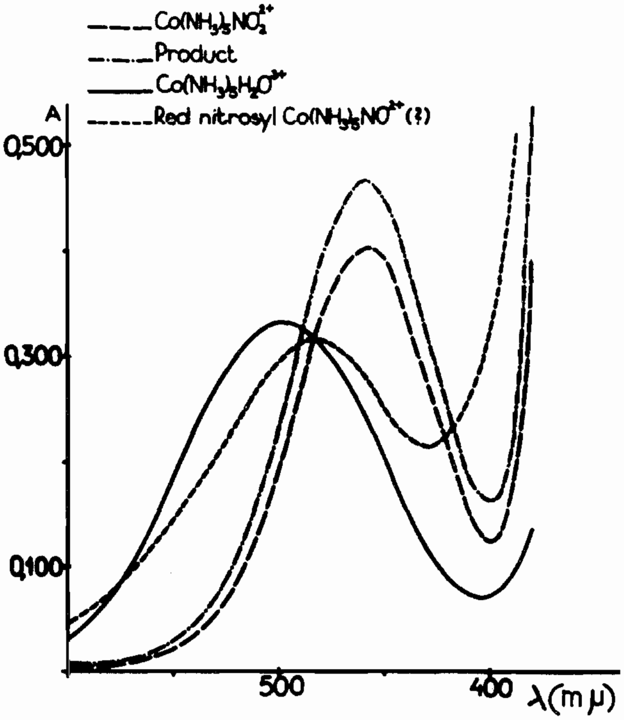

Figure 3. The spectra of the nitropentaamminecobalt(III) /— — —/, aquopentaamminecobalt(III) /———/, the red nitrosylpentaamminecobalt(III) /- - - - / complexes- and of the product of the reaction between nitropentaamminecobalt(III) complex and iodide /— · — · —/. $C_{complex} = 4{,}19.10^{-3}$ M, cell 1 cm.

There are two possibilities to explain the experimental fact that when the reaction in the nitrocomplex-iodide system apparently attains a final stage, the amount of both the iodine and NO is much smaller than stoichiometric. One has to assume either that the reaction is reversible, or that apart from the aforementioned products there is another one containing NO and some form of iodine, too. This may be a stable intermediate of the reaction. These two explanations are not substantially different, because the reversibility of the reaction is evidently due to an intermediate undergoing reactions in both directions. This intermediate may be a coordinated nitrosyl iodide. Its homolytic dissociation means the forward, while its heterolytic dissociation means the back reaction. The existence of nitrosyl iodide is proved by flashphotolysis experiments in the gas phase,[13] our experiments indicate, although do not definitely prove, its formation in aqueous solution, too. It can be expected that coordination stabilizes the nitrosyl iodide.

The experiments throw some light also on the effect of oxygen. Very careful experiments proved that the amount of iodine formed when oxygen was bubbled through the reaction mixture, was much bigger than

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(11) W. P. Griffith, J. Lewis and G. Wilkinson, *J. Inorg. Nucl. Chem.* 7, 38 (1958).
(12) R. Feltham, *Inorg. Chem.*, 3, 1038 (1964).

(13) G. Porter, Z. G. Szabó and M. G. Towsend, *Proc. Roy. Soc.*, *A270*, 493 (1962).

could have been attributed to the catalytic effect of nitric oxide evolved. This is an indication that the iodide-oxygen reaction is catalyzed by the following reactions :

$$\mathrm{Co(NH_3)_5NH_2^{2+} + I^- + 2H^+ \rightarrow}$$
$$\mathrm{Co(NH_3)_5NO^{3+} + \tfrac{1}{2}I_2 + H_2O}$$
$$\mathrm{Co(NH_3)_5NO^{3+} + O_2 \rightarrow Co(NH_3)_5NO(O_2)^{3+}}$$
$$\mathrm{Co(NH_3)_5NO(O_2)^{3+} + nI^- + nH^+ \rightarrow}$$
$$\mathrm{Co(NH_3)_5NO^{3+}} + \frac{n}{2}\mathrm{I_2} + \frac{n}{2}\mathrm{H_2O} + \frac{4-n}{4}\mathrm{O_2}$$

These experiments revealed a new possibility for the catalytic effect of inert complexes. Namely such an effect can be expected when the ligand itself has catalytic properties which are not ceased on coordination.

Reaction with azide. Each of the nitro complexes reacts with azide. The reaction is indicated by a slow change of the colour of the solution (Fig. 4) and by evolution of gaseous products. In neutral medium evolution of gases does not occur and the product is quite stable. In some cases stable solid compounds could be prepared. Their IR study is in progress. There is only a small increase in the pH during the formation of these products, even working with fairly concentrated solutions. So these intermediates cannot contain a coordinated $\mathrm{NON_3}$, the formation of which was assumed in case of nitrite-iodide reaction according to the following reaction :

$$\mathrm{HNO_2 + H^+ \longrightarrow H_2NO_2^+ \longrightarrow NO^+ \xrightarrow{N_3^-} NON_3}$$

The formation of the coordinated $\mathrm{NON_3}$ was assumed by Haim and Taube[14] in the reaction of azidopentaamminecobalt(III) with nitrite ion. This intermediate is very unstable, there is no definite proof of its existence. So it cannot be identical with the stable intermediate of the reaction of nitropentaamminecobalt(III) with azide ion. Our product decomposes in acidic medium and nitrogen and nitrous oxide are formed. We intend to make a mass spectrometric study to learn whether these two gases are formed simultaneously or successively.

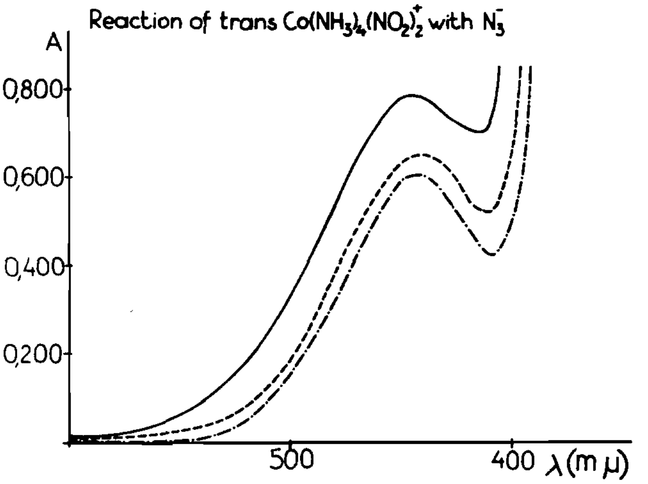

Figure 4. The spectra of the reaction mixtures of *trans*-dinitrotetraamminecobalt(III) complex and azide. $C_{\mathrm{complex}} = 5.10^{-3}$ M; $C_{\mathrm{NaN_3}} = 0{,}2$ M, cell 1 cm. —·—·—· t = 0 /no azide is present/, — — — t = 20 min., ——— t = 60 min.

The great difference in the mechanism of the reactions between the nitro-complex with the free azide, and the azidocomplex with free nitrite stresses the importance of the study of inverse reactions of this type, which can be formulated as follows:

$$\mathrm{A + B \longrightarrow I \longrightarrow P_1 + P_2 + \ldots}$$
$$\mathrm{MeA + B \longrightarrow MeI^* \longrightarrow P_1^* + P_2^* + \ldots}$$
$$\mathrm{MeB + A \longrightarrow MeI' \longrightarrow P_1' + P_2' + \ldots}$$

That is the rate and the mechanism (the nature of the intermediates and the products) of the reaction between A and B partners may change very differently if either one ore the other partner is coordinated to a metal ion.

Reaction with primary amines. The reaction of nitro complexes with sulphanilic acid was studied in presence and absence of coupling agents. The increase of absorbancy, when the nitro complex reacts with sulphanilic acid alone (Fig. 5a) clearly indicates that

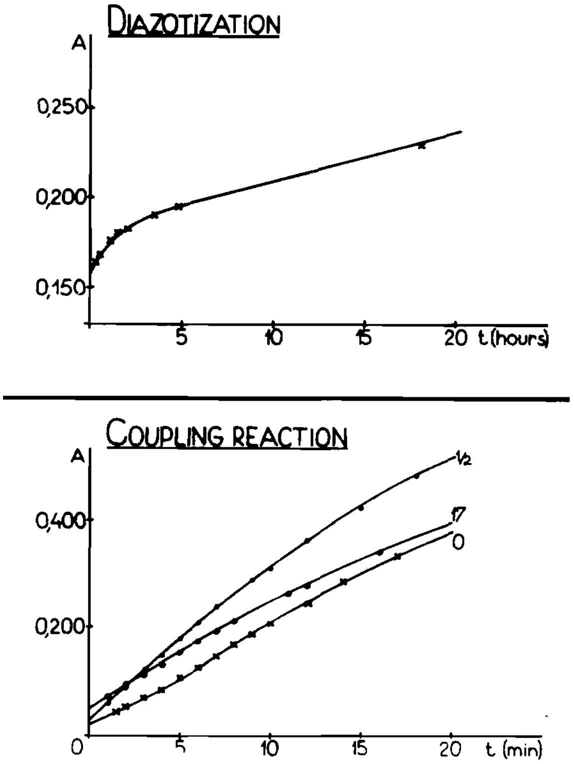

Figure 5. (a) Diazotisation of *trans*-chloronitrotetraamminecobalt(III) complex with sulphanilic acid. $C_{\mathrm{complex}} = 3{,}3.10^{-3}$ M; $C_{\mathrm{sulphanilic\ acid}} = 1{,}91.10^{-2}$ M ; $C_{\mathrm{acetic\ acid}} = 2$ M. Wavelength 425 mμ, cell. 1 cm. (b) Diazotisation/coupling of *trans*-chloronitrotetraamminecobalt(III) complex with sulphanilic acid and naphtol. $C_{\mathrm{complex}} = 5.10^{-4}$ M ; $C_{\mathrm{sulphanilic\ acid}} = 1{,}45.10^{-3}$ M ; $C_{\mathrm{naphtol}} = 1{,}82.10^{-3}$ M; $C_{\mathrm{acetic\ acid}} = 0{,}5$ M. Wavelength 480 mμ, cell 1 cm. Numbers at the curves indicate the time of the addition of α-naphtol to the reaction mixture in hours.

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(14) A. Haim and H. Taube, *Inorg. Chem.*, *2*, 1199 (1963).

the diazocompound remains in the coordination sphere. Under the same conditions and in the same concentrations sulphanilic acid and free nitrite gives a much less absorbancy. In the absorbancy versus time curve (Fig. 5a) there are two distinct stages. The first refers to the diazotisation, while the second to the further reaction of the diazocomplex: self-coupling with sulphanilic acid or elimination reactions. (Paper chromatographic experiments, the details of which will be published soon, proved that the elimination reaction is negligible in reactions with free nitrite, but it is fairly considerable with each of the nitro-complexes studied.) This appears also from Fig. 5b. In these cases the coupling agent—α-naphtol—was added to the mixture of the nitro-complex and sulphanilic acid at different time. If the coupling agent is added immediately there is a definite induction period, which disappears if the reagent is added after thirty minutes. Namely, as it appears from Fig. 5a, this time is enough to produce the diazo compound in considerable amount, which then reacts with the coupling agent. If the reagent is added after a longer time, the rate and the conversion of the coupling reaction are smaller because the concentration of the diazo derivative is diminished due to the self-coupling and elimination processes.

The rate orders obtained in the different reactions are the same with one striking exception. It appears that the substitution in *trans* position increases the ligand reactivity in general, however, in case of diazotisation/coupling reaction the relative rate is greater if the two nitro groups occupy adjacent coordination sites. The fact that in case of the reactions of *cis*- and *trans*-chloronitrobis(ethylenediamine)cobalt(III) complexes the rate order is invariably

$$\text{trans} > \text{mono} > \text{cis}$$

indicates that *the general trans effect operates in the diazotisation/coupling reaction, too, but it is overcompensated by another specific effect.* This peculiar finding can be easily explained based on the mechanism[15] of the diazotisation reaction. In the rate law the concentration of nitrous acid is on the second power, that is the reaction that is catalyzed by nitrite. So our observations show that the role of the second nitrite can be played by the adjacent nitro group.

Conclusion

The versatility of the reactions of nitrite ions and the inertness of the nitro-ammine cobalt(III) complexes make these compounds very suitable model substances for studying the effect of coordination on the reactivity of ligands in redox reactions. Although even the simplest of the systems studied is too complicated for a classical kinetic investigation, careful experiments performed under well-chosen conditions provide some important information.

Both the oxidation and the reduction of nitrite by a number of different reactants are hindered by coordination, suggesting that the observed reactivity is the resultant of several effects of opposite direction. The other ligands of coordination sphere act on the reaction of a certain ligand through their effect on the electron distribution on the whole complex (it is responsible for the general *trans* effect) and because of direct interaction between the neighbouring ligands. If the primary product of the reaction has coordination capacity, this product is withheld in the coordination sphere. This is the case in all reduction reactions. The study of the redox reactions of coordinated ligands enables us to get a deeper insight as to the mechanism of these processes and may lead to the preparation of new compounds.

(15) C. K. Ingold, Structure and Mechanism in Organic Chemistry, G. Bell and Sons, London, 1953, p. 398.