STUDIES OF SOME INORGANIC REACTION MECHANISMS

Thesis by

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To the great number of people who have made this endeavor exciting intellectually and great fun otherwise.... thanks for the memories!

ABSTRACT

Part I

The compound dihydridotetrakis (diethylphenylphosphonite)-iron(II) is known to undergo rapid rearrangement in solution. Considerable discussion has been presented to formulate a mechanism for this rearrangement. This discussion is based on a rearrangement between *cis* and *trans* dihydride isomers of octahedral stereochemistry. We present here some experimental evidence which shows the identification of one isomer (as the *trans* dihydride) is incorrect and also that the changes that occur are more complicated than the earlier workers proposed. Infrared, Raman, and very low temperature ^{1}H n.m.r. spectra of both the iron and ruthenium compounds are used to construct a different picture of this system. We identify three distinct reactions or rearrangements that are occurring and offer some proposals for the structures of the isomers. A non-classical six-coordinate structure based on a tetrahedral skeleton of phosphorus atoms about the central metal is considered the most reasonable identification of the non-*cis* isomer.

Part II

Nitric oxide undergoes many reactions to form transition metal nitrosyls of varying geometry. Under very special conditions, it then continues to react to form a species with nitrogen to nitrogen bonds. We have studied one of these reactions in detail: First, to establish the stoichiometry of the reaction exactly and second, to gain some insight into the mechanism of the dimerization step.

There is an initial rapid reaction of an ammoniacal Co(II) solution and NO with the stoichiometry one NO per cobalt(II). The NO pressure dependence of the ratio NO to cobalt is given experimentally. A qualitative proposal is made to explain this dependence, but we are still searching for a quantitative description.

There is a much slower reaction that consumes additional nitric oxide, producing N_2O and nitrite ions. If the initial cobalt(II) concentration is high, an additional product is obtained, the μ-hyponitrito bis(pentaammine cobalt(III)) ion, usually precipitated as the nitrate. The yield of the dimeric cation as a function of concentration, anion, and temperature are given. A proposal of a linkage isomerization of an unstable dimer of pentaamminenitrosyl cobalt(III) is offered to explain the experimental observations.

Part III

The decomposition of nitric oxide to elements in the gas phase is a thermodynamically favored reaction that is very slow at low temperatures (below 1000 °K). Some catalysts are known for this reaction carried out in a heterogeneous reactor. Work has been performed jointly with the chemical engineering faculty to try to understand the reaction over one of the known catalysts. The rate limiting factor is shown to be the strong inhibition by the product oxygen rather than any intrinsically slow reaction of NO. An interpretation of both our results and the results of another group is offered in terms of a unimolecular decomposition on a surface.

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GENERAL INTRODUCTION

The experimental part of a study of the mechanism of a chemical reaction consists of establishing which structures exist at various points along the reaction coordinate. Once the structures are established the mechanism of the interchange of these structures is constructed, usually by whatever argument an investigator feels is appropriate. At this point we then claim to know the mechanism of the reaction under study. We would like to know enough about the mechanisms of reactions to not only understand why and how certain pathways of reactivity are followed during a reactive encounter, but also to control and predict these pathways.

This work offers some information on three rather different areas of inorganic chemistry. A deliberate effort was made to work with problems both experimental and interpretive in the area of reaction mechanisms.

The work on the dihydridotetrakis (substituted) phosphite metal complexes was initially a problem in interpreting reported experimental observations. Only a few critical experiments are added to the previously reported data by this work, but a more comprehensive model for this system is given. This leads to some interesting conclusions about the nature of the important factors in these hydride rearrangement reactions.

The work on reactions of nitric oxide, both in solution and as a heterogeneous catalytic system, was in a more primitive state of understanding. Here only some of the gross features of these reactions were known at the start of this work. The need was for considerably more experimental information.

PART I

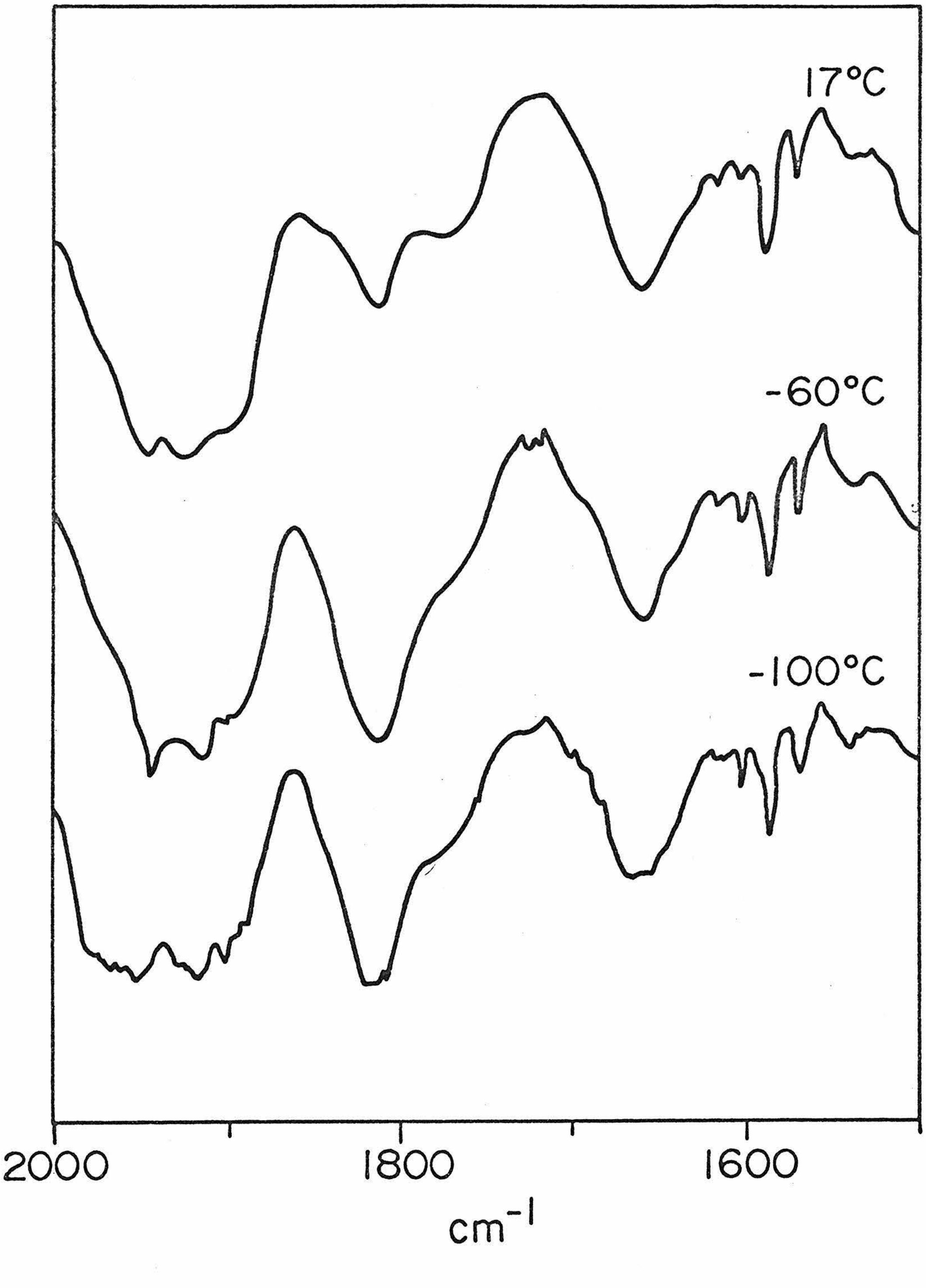
The Isomerization of Dihydridotetrakis(diethyl phenylphosphonite)Metal Complexes

Ligands containing phosphorus have been the subject of much research in inorganic chemistry for the last twenty years. The reasons for interest in these compounds range from synthetic utility to tests of theoretical predictions.[1] In this laboratory complexes of the particular ligand diethylphenylphosphonite were prepared by B. B. Chastain after initial studies suggested this ligand might have the particular mixture of σ and π bonding properties to stabilize complexes of Ni(O).[2] A. Orio prepared the iron(II) dihydride containing this ligand in 1968.[3] The low temperature ^{1}H nmr spectrum of this complex showed evidence for two species in solution whereas at room temperature an averaged spectrum or the spectrum of only one isomer was observed. Since lineshape analysis of the nmr spectrum might yield some information on the rates and, hence, the mechanism of the molecular rearrangement, further work was begun. D. D. Titus chose to study the structure in the solid to provide a basis for assigning the infrared spectrum of the solid phase.[3] As this work was finished, Jesson, Muetterties, and others at DuPont Research began publishing an extended series of studies based on an interpretation of the nmr spectrum.[4-8] We continued to think about alternative possibilities since the initial DuPont interpretation did not explain all of the nmr data and was not supported by our infrared spectra. Their most recent publications do recognize some of the points we have made, but they still have not offered a comprehensive picture of the system $H_2Fe[C_6H_5P(OC_2H_5)_2]_4$. We obtained several small but critical pieces of experimental data on this system and now wish to discuss these data and our interpretation of this problem.

When a chemist studies a "mechanism" of a chemical reaction, he (or she!) hopes to be able to describe, in as much detail as possible, the motions of all the atoms in the reacting molecules as they proceed to products. This is done in terms of energy barriers these atoms move through as the molecules break apart and rearrange.[9] In practice it is hard to collect enough experimental evidence to support or prove this detailed a picture of a reaction. We try to obtain proof of the structure of any long-lived intermediates, the reactants, and products and assume the molecules move near the minimum energy pathways on the potential energy surfaces describing the interconversion of these structures. In general, we do not obtain absolute proof of any mechanism but are content (or at least we publish) the "simplest mechanism consistent with all the observed facts".[10]

For the problem of interest an obvious important step is correctly identifying the structure of the reactants and products. D. D. Titus, in his thesis, presented the nmr spectrum at -60 °C of solutions of the compound of interest and infrared spectra of these solutions at various temperatures from 25 °C to -100 °C.[11] The infrared data is summarized in Figure 1. The DuPont workers had published more detailed examples of the nmr spectral changes in their early publications. The experimental data resulting from their work are included in Figure 2 for reference.

Figure 1. Infrared spectra of solutions of FeH_2L_4.


17°C
-60°C
-100°C
2000
1800
1600
cm^{-1}

The DuPont group originally interpreted the nmr spectra as showing the fast and slow mutual exchange limit of a cis to trans isomerization.[4,5] They then examined the nmr spectra of other similar molecules which show only the fast and slow limits of self-exchange of the cis molecule to obtain some data on the rates of the various exchange processes occurring.[6] Aspects of this work have been discussed and criticised by others.[12] In their most recent publication, the DuPont group discusses the temperature and solvent dependence of the cis/trans ratio for those cases where they see both isomers, but do not indicate how the mechanism they claim could account for the variation of this ratio.[8]

Titus argued the infrared spectrum was not consistent with a trans isomer in solution at low temperatures and offered some interesting alternatives for structures that would agree with the infrared data.

At this time we decided to look in two different directions for some additional experimental results which might give us a better idea of the processes occurring in this system. We felt the variation in relative intensity of the two isomers seen in the nmr with temperature needed additional investigation at even lower temperatures. The infrared spectrum continues to change from -60 to -100°C, and we felt that this might be a fruitful direction to look in the nmr spectrum. We also decided to look at ruthenium analogs of this compound. The infrared and nmr work on some osmium and iridium phosphine hydrides showed these complexes were rigid on the appropriate time scale for the method used.[13] We thought the ruthenium complexes might show some intermediate behavior. And the DuPont group made a comment in one of their early notes that the diethylphenylphosphonite ruthenium(II) dihydride existed as both cis and trans isomers.[4]

Experimental Details

The synthesis of the ligand diethylphenylphosphonite and of the complex of this ligand with iron(II) is described in great detail in the thesis of D. D. Titus.[3] The DuPont workers give some details of the synthesis of the ruthenium complex, but the method and the products differ in some aspects from this work.[7] The ruthenium complexes were synthesized starting from commercial "$RuCl_3 \cdot 3H_2O$". This material is mostly Ru(IV) oxy-or hydroxychloride.[14] Only occasional lots of the starting material would give the desired complex if this material was simply substituted for the $FeCl_2$ in the recipe of Titus.

There are several methods in the literature that are supposed to convert the $RuCl_3 \cdot 3H_2O$ to Ru(III). One method is to evaporate the material with ethanol.[15] This had no effect on attempts to prepare the complex from those portions of the starting material that gave no complex without this treatment. It is also possible to reduce all of the Ru(IV) to Ru(III) by refluxing an HCl solution of the "$RuCl_3 \cdot 3H_2O$" over elemental mercury.[16] 6.5 grams of Matthey-Bishop $RuCl_3 \cdot 3H_2O$ was dissolved in 200 ml. of 3N HCl. 5 ml. Hg was added and N_2 was flushed through the solution for 30 minutes. Then the apparatus was closed off with anti-suck-back Hg bubbler and the mixture refluxed overnight. It was cooled under N_2 and filtered. The filtrate was dark green. The solution turned dark red after a day. This is mentioned in the literature.[16] Then the solution was evaporated to dryness under Ar. The solid was black and readily soluble in ethanol to give a dark green solution. Exposing the dark green solution to air caused it to turn purple very rapidly. The dark green solution proved satisfactory for synthetic purposes. However, since other attempts to reduce ruthenium compounds with mercury have resulted in complexes containing both metals, alternative procedures were tried.[17]

One very convenient method is to pass hydrogen gas through a hot (70-85 °C) solution of "$RuCl_3 \cdot 3H_2O$" in dilute HCl.[18] This solution was then evaporated to dryness and the resulting solid dissolves readily in ethanol. This also proved satisfactory for synthetic purposes. A typical synthesis starting with the ethanolic solution of Ru(III) is described: The syntheses were carried out always protected from oxygen using either Ar or N_2. A slight excess of phosphine ligand was added to the ethanolic solution of the metal and refluxed for at least 8 hours. A brownish, curdy, precipitation occurred and redissolved to a dark green solution. A small excess of sodium borohydride in ethanol was added to the reaction after cooling to room temperature. The solution would slowly turn orange to yellow. Sometimes it helped to heat the solution after adding the borohydride. After the solution became light colored it was filtered and the filtrate stored at 5 °C. After several days, crystals were seen. They were white to slightly orange. Crystals grew very slowly for weeks. The yield of crystals, based on Ru, was low (never more than 25%). The solution did not lose much color, so it appears much of the Ru complex remains in solution. Analytical Data: Theoretical C, 53.6; H, 6.98. Found C, 53.4; H, 7.05.

The DuPont group reported a synthetic procedure somewhat similar to this procedure up to the point of obtaining the light yellow colored solution. At this point, they did not wait for crystals but evaporated the solvent to obtain an oil which they separated by column chromatography. They took a yellow fraction and evaporated the solvent to obtain a "semi-solid". From this they obtained crystals with methanol.[7]

Infrared spectra of solid samples were obtained as mineral oil mulls on KBr plates. Solution spectra were obtained in methylcyclohexane solutions with a 0.1 cm pathlength cell with AgBr windows. This cell was mounted in a low temperature dewar for measurements below room temperature. For solid spectra at low temperatures, both the KBr pellets and mulls on pure KBr pellets were placed in the dewar.

Raman spectra of the solids were obtained in the usual fashion by pressing the solid against the lens of the spectrometer. We attempted to obtain solution spectra, but no peaks other than solvent were ever observed.

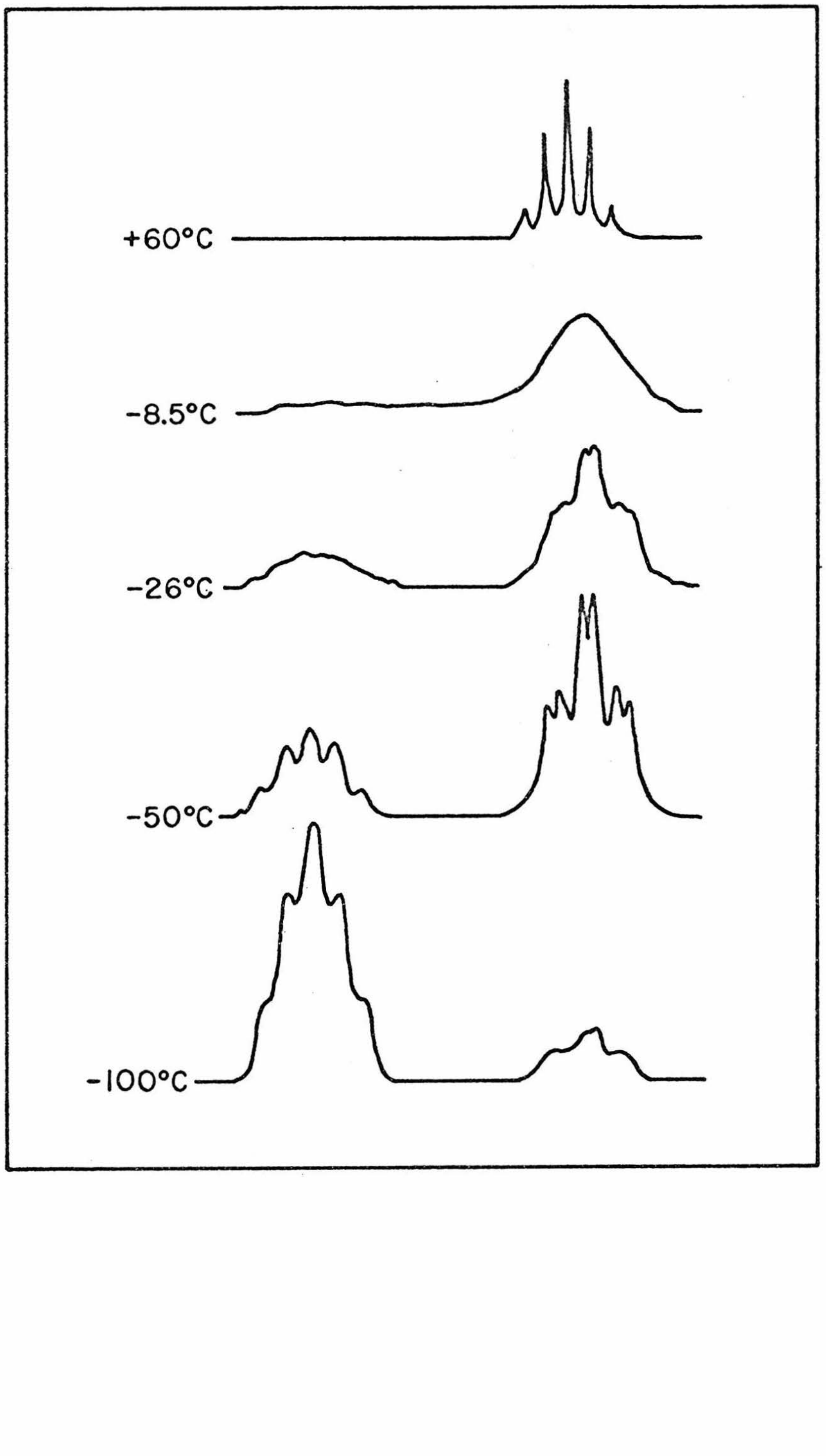
Nmr spectra of both the iron and ruthenium complexes were obtained on methylcyclohexane solutions from -60 °C to +50 °C on a

Varian Model HR-220 spectrometer. These are identical to those reported by the DuPont group. An attempt was made to observe the ^{1}H nmr spectrum of the iron isomers at some temperature lower than -65 °C. A spectrum was observed at approximately -100 °C with the help of Dr. Stanley Manatt at the Jet Propulsion Laboratory on a modified Varian Model HA100 spectrometer.[19] The spectrum was not recorded but observed on an oscilloscope. A sketch was made of the spectrum in a laboratory notebook. While the absolute areas are not accurately represented, careful attention was paid to relative peak intensities and linewidths. The sketched spectrum is reproduced as the -100 °C spectrum in Figure 2.

Results and Discussion

First we wish to point out the time scale sensitivity of the various experimental measurements used in this study. Since some of the conclusions rest on the observation of a particular species by one method and not by another one, we need to have a clear picture of the basis for these assignments. We first restrict our attention to consideration of molecules which rearrange identical nuclei. (If non-identical nuclei rearrange, the identification problem is usually much easier--see later.) Now for the purpose of explanation by example, we choose infrared spectroscopy. Consider the effect on the infrared spectrum, if a molecule maintains a fixed geometry of nuclei (with respect to a given structure) and simply vibrates in the usual assortment of normal modes and, in addition to these motions, once each second permutes all of its identical nuclei. Except for the

Figure 2. NMR spectra of solutions of FeH_2L_4 at various temperatures.


+60°C
-8.5°C
-26°C
-50°C
-100°C

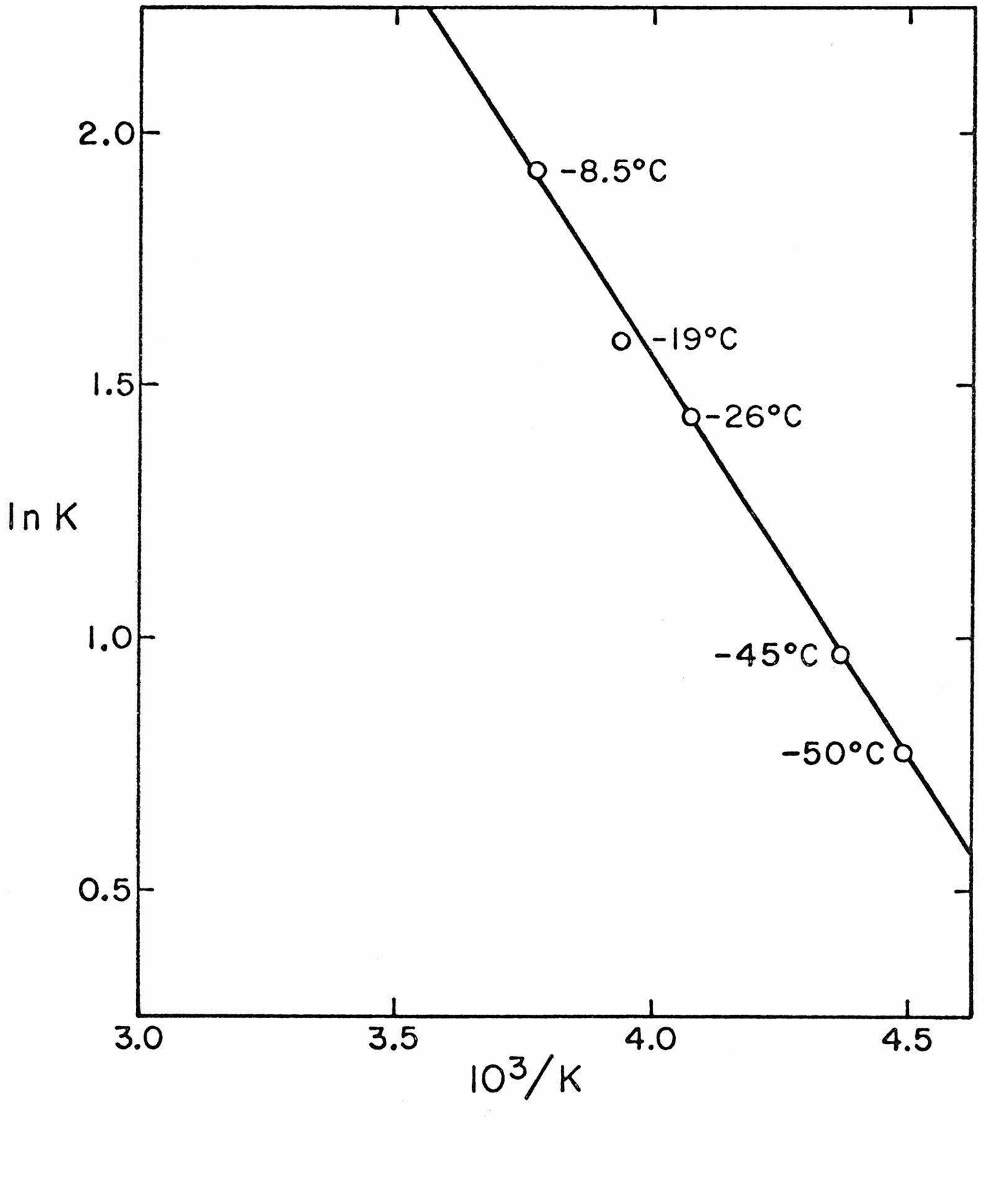
time needed for the permutation, the molecule produces the identical spectrum on both sides of the permutation. If the permutation is very fast (say 10 times smaller) compared to the time needed for a quantum or one wavelength of infrared radiation to pass across and interact with the molecule, then the permutation will have essentially no detectable effect on the infrared spectrum of the collection of molecules in the sample. This reasoning then allows a simple calculation to be made giving the approximate rigid-time needed for various experimental measurements. Such a table can be found in many places in the literature.[20] Since we would expect the fastest time possible for a permutation of nuclei to occur would be about the time needed for a vibration of a molecule, it seems unlikely we could observe effects of rearrangements on infrared linewidths. For nuclear magnetic resonance experiments, electron resonance and quadrapole resonance experiments, the opposite is true.[20] Here, because the usual frequencies of interaction are 10^6 (or more) times longer than for UV-visible-infrared spectroscopy, many examples are known of permutational effects on lineshapes.[21] Our approach for the present problem was to use infrared spectroscopy to examine a rearrangement that is slow on the nmr time scale to answer some of the uncertainty in interpretation of the nmr spectrum.

Examination of the infrared spectrum of H_2FeL_4 (where L = diethylphenylphosphonite) and comparison of the infrared and nmr spectra over the temperature range shown in figures 1 and 2 lead to the following conclusions:

Above about 0 °C there is only one isomer present in any significant concentration with approximately the cis dihydride configuration of octahedral stereochemistry similar to that found in the solid.[22] The nmr spectrum above about 30 °C shows all the P atoms appear equivalent to each of the H nuclei and therefore the rearrangement consists of permutations of nuclei about the cis dihydride structure. The very weak infrared band at 1929 cm^{-1} at room temperature which splits into two weak bands around -100 °C at 1920 and 1965 cm^{-1} is assigned to ν_{as} Fe-H.[22] (The splitting of the band at the very low temperature is thought to be the result of the disappearance of the cis isomer, in the reaction discussed later, with the ligand spectrum then giving rise to the two observed bands.)

As the temperature is lowered, two species are seen in both the infrared and nmr experiments. This must be due to an isomerization equilibrium in which the equilibrium constant changes over the temperature region studied to the extent that the relative amounts of the two isomers becomes about equal at -50 °C. It was to prove this point the -100 °C nmr spectrum was obtained. It was expected that the relative intensities would continue to change as the temperature was decreased. Since the relative intensities should be in the same proportion as the concentrations of the two isomers, we measured the areas under the peaks for the isomers in the range -8.5 °C to -50 °C and took the ratios of the areas to be the equilibrium constants. Figure 3 shows a plot of ln K vs $10^3/T$. The points lie reasonably close to a straight

Figure 3. Temperature dependence of the isomerization equilibrium constant.


2.0
1.5
1.0
0.5
ln K
3.0
3.5
4.0
4.5
$10^3/K$
-8.5°C
-19°C
-26°C
-45°C
-50°C

line. The thermodynamic variables derived from the plot for the reaction:

$$\text{low temperature stable isomer} \rightleftharpoons \underline{\text{cis}}\ \text{isomer}$$

are found to be:

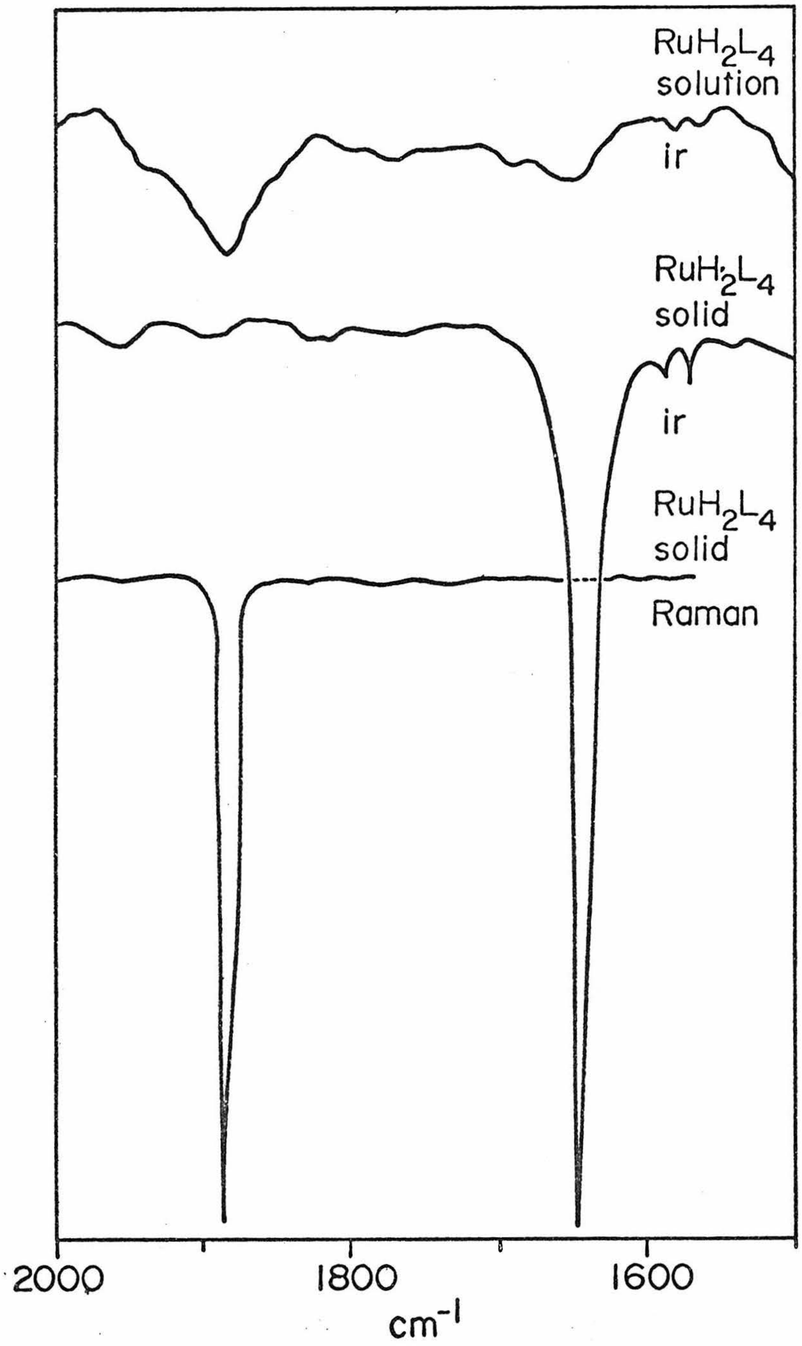
$$\Delta H = +3,120 \pm 150 \text{ calories/mol.}$$

$$\Delta S = +15.6 \pm 1.0 \text{ entropy units}$$

The isomer which appears in significant concentration only at low temperatures does not contain the trans dihydride metal structure. Trans dihydride species have been studied both in solids and in solutions by infrared spectroscopy.[23] These compounds have sharp, quite intense absorption bands in the region 1600 to 1750 cm^{-1}, about 200 to 400 cm^{-1} lower energy than the cis dihydrides. Since we would expect to observe even a small amount of trans isomer in the solution and, at -50°C where the concentration of the second isomer is large, we do not see a band characteristic of the trans isomer, consideration of alternative structures is appropriate.

The fact that no trans dihydride isomer is present is reaffirmed upon examination of the infrared and Raman spectra of solid H_2RuL_4. These are shown in Figure 4. Also in Figure 4 is the infrared spectrum of a dilute methylcyclohexane solution of the complex. The solid exhibits the spectrum expected for a trans dihydride. ν_{as} Ru-H is a sharp and very intense band centered at 1643 cm^{-1}. The Raman spectrum shows ν_{sym} Ru-H at 1886 cm^{-1} also sharp and intense.[24] A structure determination of this complex has shown it to be the trans isomer.[25] The DuPont group

Figure 4. Infrared and Raman spectra of RuH_2L_4.


RuH_2L_4
solution
ir
RuH_2L_4
solid
ir
RuH_2L_4
solid
Raman
2000
1800
1600
cm^{-1}

reports only weak infrared bands at 1895 cm^{-1} and a shoulder at 1950 cm^{-1}.[7] Their crystallization method appears to have extracted only the cis isomer.

The solution spectrum at room temperature does not show the characteristic trans dihydride band, however. Other ruthenium dihydrides have been found to retain the trans infrared band in solution, so we concluded that in solutions of this complex some other structure is move favorable.[23] The DuPont group show these solutions contain only about 5 to 7% trans (by nmr assignment).[8] The infrared spectrum does not change on cooling, in contrast to the iron complex spectra. We could not obtain solutions of the complex concentrated enough to observe the trans isomer in the nmr spectrum. We did observe the cis dihydride pattern as reported by others.[13a]

This is obviously a complex system. We can observe two distinctly different isomers of a six coordinate complex and see evidence for intramolecular exchange in one, and possibly both, of these isomers. One route to understanding the processes occurring is to establish the structure of each isomer observed and then look for pathways to rearrange each isomer to itself (virtual exchange) and to interchange the structures (isomerization).

There is little question about the identity of one isomer. The species in solution at room temperature and giving the six line nmr spectrum at -50 °C is the cis dihydride of octahedral stereochemistry.

The infrared of the solid and solution is nearly identical, and the solid structure is known. The six line spectrum has been shown to be consistent with a cis dihydride structure.[7]

The structure of the other isomer is not so easily established. There are two experimental results to consider, the nmr spectrum and the infrared results. The ^{1}H nmr spectrum, a quintet with a 1:4:6:4:1 intensity distribution, is consistent with a trans dihydride structure as suggested in the earlier work.[4] However, this spectrum is also expected for an isomer undergoing rapid virtual exchange (an example is the cis isomer at high temperature). The ^{31}P nmr spectrum of the low temperature stable isomer is an unresolved broad peak even when the cis isomer is in the slow exchange limit, supporting the possibility of considerable motion in this isomer even at -50 °C.[5] The infrared spectrum eliminates the trans isomer as a possibility. Specifically, the infrared spectrum indicates the H-M-H subunit must be quite similar to the cis configuration.

There are many possible structures of octahedral stereochemistry if we consider all the distortions (trigonal, tetragonal, tetrahedral subunits, etc.). Since all we can actually say is that it must be somewhat different from the cis dihydride known in the solid and appears able to undergo (intramolecular) exchange rapidly even at -100 °C, we can only suggest the most likely structure. We think the most likely structure is one which has the four P atoms in tetrahedral coordination about the metal ion, with the hydride ions located on two faces of the tetrahedral MP_4 unit.[7] While this structure is not one of the usually recognized forms of octahedral stereochemistry, there are three reasons to consider it:

1. The MP_4 unit in the solid is distorted considerably toward a tetrahedral structure. The phosphorus motion needed to convert the cis isomer to the "tetrahedral" form is quite small. To convert the cis isomer to a trans isomer would require a much greater phosphorus motion.

2. The exchange of the hydride ligand from one tetrahedral face to another would require only very small phosphorus motion, and therefore the hydride exchange could continue to very low temperatures.

3. The H-M-H angle in the "tetrahedral" isomer would be ~109° and might be expected to exhibit a weak infrared stretching absorbtion near the cis (90°) stretch, but displaced towards the trans (180°) absorption, as observed.

It is interesting to consider the analysis of the nmr spectrum of $FeH_2[P(OC_2H_5)_3]$.[7] This was interpreted as showing the fast and slow exchange limiting spectrum of a cis dihydride of distorted octahedral stereochemistry. Using a "jump" model calculation, the authors showed only certain kinds of permutations of the phosphorus and hydride ligands would give good agreement to the observed spectrum. The exchange process was shown to be consistent with the motion of the hydride ions about the central ion being principally responsible for exchange of the H-P coupling, with some motion of the phosphorus to preserve the distorted octahedral structure. One consequence of this process is the outer two lines of the spectrum remain sharp through the transition from the fast to slow exchange limits. In discussing possible intermediates in the exchange, a tetrahedral MP_4 subunit with hydride ions on two faces of the tetrahedron was considered most reasonable.

A description of the behavior of the complex $FeH_2(C_6H_5P(OC_2H_5)_2)_4$ can be given using the model developed above. At +50 °C, a cis dihydride undergoes virtual exchange through an intermediate containing an MP_4 tetrahedral subunit. As the temperature is lowered, this intermediate becomes a stable isomer, and an isomerization occurs. When the temperature falls to -50 °C, several changes have occurred:

The exchange reaction of the cis isomer has slowed so that each isomer exists long enough to exhibit the slow exchange limiting nmr spectrum.

The isomerization reaction occurs less often and the nmr experiment shows the two isomers in solution.

The other virtual exchange reaction, rearrangement of the hydrides about the MP_4 tetrahedral unit, is still occurring rapidly enough to show only fast exchange limiting spectrum.

If we use this model to explain the behavior of $Fe_2[C_6H_5P(OC_2H_5)_2]_4$, we can discuss the behavior of a series of substituted phosphine dihydrides as reported by P. Meakin, et al.[6] In general, there is an intramolecular isomerization reaction occurring through an intermediate with a much higher energy than the products or reactants, and therefore the intermediate is not detected. When the ligand is $C_6H_5P(OC_2H_5)_2$ or $C_6H_5P(OCH_3)_2$, the intermediate is stable at low temperature, and is detected. When the intermediate is stable, the jump model must now contain a third structure. Since this structure contains P-H coupling constants different from the end members of the scheme, broadening of all the lines are expected as the intermediate lifetime becomes longer. This is observed.

Finally, we can consider the factors that determine whether an intermediate is observable. Considering the ΔS term we see that it favors the cis isomer. From model building using space filling (CPK) models and approximately octahedral central ion distances vs. a tetrahedron with slightly shorter central ion distances, it appears the ligands are more constrained to only one conformation (if they fit at all, see later) in the tetrahedral isomer. In the octahedral model there are more possibilities for rotation of the alkyl groups, for example, of the phosphite ligands. For the general case we assume the ΔS term will always favor the cis isomer, that is, the ΔS term will be about constant for all the complexes considered by the DuPont group.[6]

There are several factors to be considered in the ΔH term. First, there might be some fairly important electronic factors favoring the tetrahedral dispositions of the phosphorus atoms about the central metal. These could be related to the varying σ and π bonding capabilities of the various ligands. The relative size of this term could be a factor in determining if the total ΔH term will be favorable enough to overcome unfavorable steric contributions to the

ΔH term and the unfavorable ΔS term. In addition, a conclusion from our model building is there are some ligands for which steric crowding would be so great as to make the ΔH term unfavorable and hence the tetrahedral form might never become a stable isomer.

For the ligand $C_6H_5P(OC_2H_5)_2$ we find the cis dihydride isomer actually more crowded sterically than the tetrahedral isomer. For the ligand $C_6H_5P(OCH_3)_2$ the complex is more crowded in the tetrahedral form than the isomer with the ethoxy groups, but still less crowded for the cis than the tetrahedral. Thus for these ligands we might conclude the enthalpic preference for the tetrahedral form is a consequence of only steric factors, if the electronic factors contributing to the ΔH term are constant for all the ligands.

We think that more interesting details of this system and similar systems are ready for investigation. Certainly some of the data extracted from the previous work on linewidths and energies of some of these processes is still valid. Now with a more consistent picture of the overall reaction occurring we can hope to design experiments designed to provide data on other details of this system.[26]

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22. Reference 3, Section II, p 49.

23. D. N. Adams, *Metal-Ligand and Related Vibrations*, St. Martin's Press, New York, 1968, Chapter 1.

24. The appearance of the symmetric mode at higher energy than the asymmetric mode is consistent with the strong trans influence of the hydride ligand. The asymmetric stretch involves lengthening one Ru-H bond while shortening the other one, which should be energetically favorable relative to symmetrical stretching for a strong trans directing group.

25. L. J. Guggenberger has communicated to us that he has determined the structure of crystalline H_2RuL_2 by X-ray techniques and found the stereochemistry to be trans-octahedral.

26. A paper based on the work discussed here has been accepted by the American Chemical Society Journal for publication in July of 1973.

PART II

The Reaction of Nitric Oxide with Cobalt Ammine Solutions

Nitric oxide is a thermodynamically unstable chemical compound. The free energy change, under standard conditions, for decomposition to elements is -20.719 kcal $mole^{-1}$.[1] The entropy change is quite small, only 2.95 cal deg^{-1}, so the difference in free energy between NO and elemental N_2 and O_2 is mostly due to the bond strength differences. Yet this reaction is unknown in the gas phase at room temperature, leading to an estimate that the activation energy is greater than 50 kcal $mole^{-1}$ at 25 °C.[2]

The nitric oxide molecule has an unpaired electron and is a moderately reactive species in many reactions. It is oxidized to NO^+ and reduced to NO^- quite readily.[3,4] It forms a very large number of addition compounds with transition metal ions.[5,6] It does form a dimer in the gas phase, although the equilibrium constant is quite small.[7] The structure of the dimer is thought to be ONNO with a bent _cis_ stereochemistry.[8,9] The dimer does not seem to decompose to elements.

We might speculate why the decomposition to elements does not occur. There has been a great interest in discussing reasons for chemical reactivity of small molecules using simple molecular orbital theory.[10] For this reaction,

$$2NO \rightarrow N_2 + O_2 \qquad (1)$$

we can start on a much simpler level and then look at more elaborate explanations.

If the reaction is to take place with the standard free energy change, we must consider the molecules in their electronic ground states for the conversion of reactants to products. The ground state terms are: NO, $^2\Pi$; N_2, $^1\Sigma$; O_2, $^3\Sigma$.[11]

We see that spin angular momentum is conserved in reaction (1) since there are two unpaired electrons on each side of the reaction. However, orbital angular momentum is not conserved. The excited states of N_2 or O_2 with enough angular momentum to allow the reaction by this selection rule are so high in energy the reaction is thermodynamically unfavorable.[12]

These considerations show why a concerted reaction does not occur. More elaborate considerations of this point can be constructed using the symmetry of the molecular orbitals involved, such as that of Pearson's HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) method, or by state correlation diagrams.[13,14]

If non-concerted reactions are considered, the problem is more complex. We first consider the formation of the dimer ONNO. The nonexistence of this species has been the topic of considerable discussion because it is often used to point out the applicability of various bonding models.[15] The molecule NO has the one unpaired electron in a Π antibonding orbital. The next four electrons are in a doubly degenerate Π bonding orbital. The lower lying electrons form two σ bonding and one σ antibonding orbital.[16] The bond order for NO is then two and one-half. For the dimer, there would be five bonds total (two nitrogen to oxygen; one nitrogen to nitrogen) so there would be no change in total number of bonds upon dimerization. The reaction:

$$(NO)_2 \rightleftharpoons 2NO$$

is estimated to have an equilibrium constant of approximately 1300 atm. at 298 °K.[7] Under pressures of 200 to 400 atm. and in the range 30° to 50°C, NO decomposes according to:[17]

$$3NO \rightarrow N_2O + NO_2 \qquad (2)$$

although this is thermodynamically less favored than other reactions[2]:

Reaction	ΔG°_{298} kcal
$4NO \rightarrow N_2 + 2NO_2$	-57.8
$2NO \rightarrow N_2 + O_2$	-41.3
$4NO \rightarrow O_2 + 2N_2O$	-32.7
$3NO \rightarrow N_2O + NO_2$	-24.6

Melia showed that the experimental rate of reaction (2) was consistent with third order kinetics[17]:

$$\frac{-d[NO]}{dt} = k[NO]^3.$$

The variation of the rate with temperature and pressure was also consistent with the mechanism in which the dimer was formed and then reacted with an additional NO molecule. At 400 atm. NO pressure and, using the equilibrium constant given by Billingsley and Callear, we calculate that the dimer should be the predominant species in that system.[7] The reaction is still quite slow (as might be expected by reasoning used earlier about spin and angular momentum being conserved) and the reaction is run in an autoclave where we cannot be sure it is entirely a gas phase reaction.

The empirical observation is, therefore, that even under conditions where the dimer could exist in high concentration no reaction attributable to a dissociative mechanism of the type:

$$2NO \rightleftharpoons ONNO$$

$$ONNO \rightarrow ONN + O$$

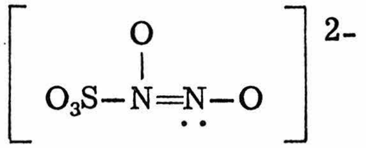
or

$$ONNO \rightarrow N_2 + 2O$$

is observed. Of course, the above reactions are rather obviously unfavorable considering the relative stabilities of O and O^- in the gas phase. Other mechanisms, such as those forming NOON or ONON in the first step are considered less likely since no evidence for the existence of these dimers has been reported.

If we now look beyond homogeneous gas phase reactions, we find some very interesting possibilities. We can find reactions of nitric oxide which do not go all the way to N_2 and O_2 but do proceed to compounds which link together the nitrogens to make multiple N-N bonds. This must certainly be an important part of any system of reactions to carry out reaction (1) in a multiple step path.

The oldest of these reactions is probably the reaction observed when NO is passed through a solution of alkaline sulfite to give the following ion:



$$\left[O_3S-\overset{\overset{O}{|}}{N}=\underset{\cdot\,\cdot}{N}-O \right]^{2-},$$

N-nitrosohydroxylamine-N-sulfonate.[18] This compound can be easily isolated as a crystalline salt.[19]

With some organic ammines a similar complexed hyponitrite derivative can be formed[20]:

$$2R_2NH + 2NO \rightarrow [R_2NN_2O_2] + R_2NH_2{}^{+}.$$

And there is a preparative method for hyponitrites using sodium in liquid ammonia[21]:

$$2Na + 2NO \underset{LNH_3}{\rightarrow} 2Na^{+} + N_2O_2{}^{2-}.$$

Getting a little more complicated with reactions giving several products, we find the reduction of NO by the aqueous electron giving[22]:

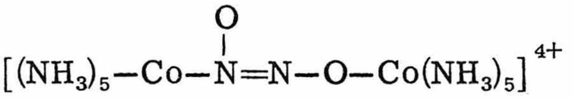
$$e^{-}_{aq} + 3NO \xrightarrow{H+} HNO_2 + N_2O.$$

There is also the copper(I) catalyzed reduction of nitric oxide by tin(II) chloride[23];

$$2NO + Sn(II) + 2H^{+} \rightarrow N_2O + Sn(IV) + H_2O$$

As another example we come to the reaction observed by Sand and Genssler and later studied by Werner and Karrer between nitric oxide and the popular ammoniacal Co(II) solution.[24, 25] In this reaction a variety of products is produced. It is mentioned in the literature that both a red and black isomer of the empirical formula

$[Co(NH_3)_5NO]_x^{(2x)+}$ is formed. The structure of these isomers has been settled to a great degree by recent X-ray diffraction studies.[26, 27] The black isomer is the monomeric ion containing the NO^- group, isolated as the chloride, $[Co(NH_3)_5NO]Cl_2$. The red isomer has a most unusual structure;



$$[(NH_3)_5-Co-\overset{\overset{\displaystyle O}{|}}{N}=N-O-Co(NH_3)_5]^{4+}$$

and is usually obtained as the nitrate. There are several reports of chemical properties, syntheses, and reactions of these isomers in the literature, and a proposed mechanism for this particular isomerization.[28]

Since there was actually very little experimental work on this reaction to support the proposed mechanism and there were several contradictory results in the paper of Gans on this subject, we decided to extend this work studying the isomerization reaction.

This reaction was also of interest because of the parallel interest in the gas-solid reaction of NO over Co_3O_4, as reported elsewhere in this thesis. It is stated that under some conditions the red isomer can be decomposed thermally to give N_2, at least.[29, 30] We therefore harbored the desperate hope that by studying the reaction in solution perhaps we might then transfer some niggling idea to help run the gas-solid reaction more to our liking. We would then have a satisfactory catalyst for a reaction that is thermodynamically favored but kinetically slow. This is one of the most sought after demonstrations of an inorganic chemist's ability to master the art of chemistry.

In addition to this noble goal, there is much practical interest in this general problem applied to nitric oxide.[30]

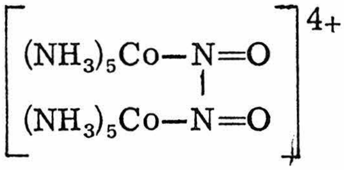
The mechanism of the reactions leading to the red and black isomers of pentamminenitrosylcobalt(III) seemed to offer an interesting demonstration of what G. N. Schrauzer suggests are the three primary functions of catalysts:

> "1. Catalysts increase reaction rates by their ability to relax restrictions of quantum mechanical selection rules of spin and angular momentum.
>
> 2. Catalysts bring reacting particles together in energetically and sterically favorable fashion.
>
> 3. Catalysts introduce effective alternative reaction pathways."[31]

If we ever understand what is going on in this system, it will serve as a beautiful example of all of these principles. Until that time, however, we have to consider the experimental results.

General Discussion of Previous Work on the Pentaamminenitrosyl cobalt(III) Complexes

The structures, oxidation state, and chemistry of the red and black isomers of pentaamminenitrosylcobalt ions have been the source of considerable controversy following Werner and Karrer's original assignment of structures.[25] They thought, based on color and reactivity, the red isomer was dimeric with a bridging hyponitrite group:



$$\left[\begin{array}{l}(NH_3)_5Co-\underset{|}{N}=O\\ (NH_3)_5Co-N=O\end{array}\right]^{4+}$$

while the black salts were simple monomeric coordination compounds. At the start of this study preliminary accounts of the crystal structure determinations of both isomers had appeared and shown these guesses to be essentially correct.[26,27] We will therefore not follow in detail all the intermediate incorrect assignments and assertions of structures. However, several problems did still exist in interpreting the magnetic data and infrared spectrum for the black isomer, and the synthetic route to the red isomer was not very clearly defined.

In the most careful appearing studies of the infrared spectrum of the black isomer, an extra band was always observed and attributed to $Co(NH_3)_6Cl_2$. In addition, the magnetic properties seemed to be somewhat variable. Since this is assigned as a Co(III) compound, one would expect it would be diamagnetic but with a temperature independent susceptibility due to the second order interaction of the ground and excited electronic states. This should amount to about $+200 \times 10^{-6}$ cgs units or so.[32] Reported values of the susceptibility ranged from diamagnetic to slightly paramagnetic. These problems occur because analysis of the solid is difficult. Analysis for Co, NH_3 (or N_2), or Cl cannot be used to distinguish between mixtures of $Co(NH_3)_6Cl_2$ and $[Co(NH_3)_5NO]Cl_2$ and pure $[Co(NH_3)_5NO]Cl_2$. Ten percent of the hexaammine in the nitrosyl still provides an acceptable analysis for pure nitrosyl.

The possible synthetic routes to the red isomer also were not consistent with some of the properties reported for the chemistry of the compounds. Some of the methods suggested that the red compound was made in the presence of air at room temperature, while others say the red compound is made from the black salt.[33, 34]

Thus, our initial efforts would be to try to understand some of the chemistry of the syntheses of the various isomers to provide a basis for deciding on how to proceed to study the mechanism of the dimerization reaction.

There is a published mechanism for this dimerization.[28] It is based on some observations on the reactivity of the black isomer and the yield as a function of temperature of the red isomer. It does provide a starting point for testing various reactions as steps in the reaction and for that reason is worthwhile discussing in some detail.

The sequence of reactions is proposed to be:

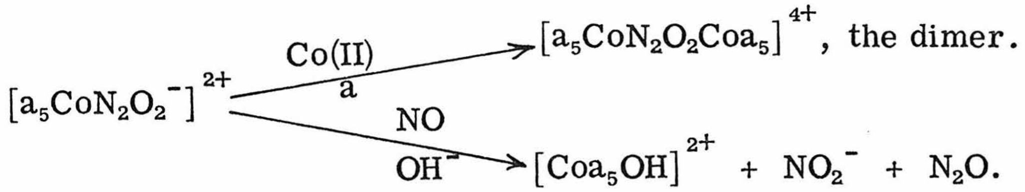
$$\mathrm{NO} + \mathrm{Co(II)} \overset{\mathrm{a,\,xs}}{\rightleftharpoons} [\mathrm{a_5CoNO}]^{2+} \qquad (3)$$

where a is ammonia and the monomer is Co(III) and NO^-.

Then,

$$[\mathrm{a_5CoNO}]^{2+} + \mathrm{NO} \rightarrow [\mathrm{a_5CoN_2O_2}^-]^{2+} \qquad (4)$$

This can react by two paths:



$$[a_5CoN_2O_2^-]^{2+} \xrightarrow[a]{Co(II)} [a_5CoN_2O_2Coa_5]^{4+}\text{, the dimer.} \qquad (5)$$

$$[a_5CoN_2O_2^-]^{2+} \xrightarrow[OH^-]{NO} [Coa_5OH]^{2+} + NO_2^- + N_2O. \qquad (6)$$

The first reaction, (3), is known to be reversible, since attempts to dissolve the black chloride in an ammonium hydroxide solution or even a neutral water solution cause it to quickly decompose to Co(II) hydroxide and NO is evolved. The yield of dimer is low, usually not greater than 25%, and is zero at 7 °C or at 40 °C. The maximum yield is obtained between 20 ° and 30 °C. N_2O is detected as a gaseous product over the reaction at various temperatures, and NO_2^- was found in the solution by Gans.

Gans supposed the yield of dimer varied with temperature because of reaction (3). Below 7 °C it went essentially to completion and there was then no reaction (5), only reaction (6). At high temperatures reaction (3) did not yield enough monomer for further reaction, and therefore, no reaction occurred.

Before doing any experimental work, several points in the proposed mechanism were questioned. First, it seemed unlikely that reaction (3) would go from 100% completion to essentially zero over a temperature change of 33 °C. Second, the $N_2O_2^-$ ion has not been invoked in any mechanism for the previously mentioned reactions of NO. Third, this dimer was reported only when nitrate was the anion. This seemed curious, and NO can reduce HNO_3 to HNO_2, and that may therefore by the source of the NO_2^-.[35]

This was the "state of the art" at the time we began to try our hand at the various synthetic reactions. In addition, we planned to devise some experimental test of the equilibrium reaction (3) as a function of temperature and NO pressure. If we could sort out the analytical problems, the stoichiometry of the overall reaction at various temperatures would be determined. Then, provided we could find a system where no insoluble species interfered and we could control the yield carefully, we might be able to extract some kinetic parameters from the various measurements. And then make a guess at a mechanism.

The Black Isomer

Monomeric nitrosylpentaamminecobalt(III) complexes can be isolated by bubbling NO through solutions of Co(II) in ammonium hydroxide. If the temperature is kept below about 10 °C and an anion which gives a relatively insoluble salt is present, the compound precipitates and is easily filtered off. Air must be excluded because it will oxidize the NO and produce nitrite and nitrate anions in this solution. These will substitute in the coordination sphere of the Co(II) which is also oxidized by the air, producing undesired Co(III) nitro, nitrito, and nitrato complexes.

This preparative scheme works very nicely but there is a distinct problem with it. If NO is not bubbled through this solution, this recipe is a reasonable preparative route to $Co(NH_3)_6^{2+}$.[36] Two articles in Inorganic Syntheses describe the preparation of the monomer chloride; the first does not recognize the problem with the hexaammine, the second article corrects the method for this problem by working in more dilute ammonium hydroxide and using an extra purification step.[37,38] It is this impurity hexaammine which was resonsible for the variable magnetic properties reported for this compound.

The infrared spectrum of this complex has been the subject of considerable study due to interest in the N–O frequency as a measure of the formal oxidation state of coordinated nitrosyl.[34,39,40] This problem had been essentially solved several years ago, but even in this work an anomalous band at 1172 cm^{-1} was observed and dismissed as an impurity.[40] The assignment of this anomalous band at 1172 cm^{-1} as the hexaammine Co(II) is based on a reasonable argument. In most hexaammine metal complexes the δ_s motion of the coordinated ammonia molecules occurs between 1091 cm^{-1} ($Cd(NH_3)_6Cl_2$) and 1370 cm^{-1} ($Pt(NH_3)_6Cl_4$).[41] In $Co(NH_3)_6^{3+}$ it is observed at about 1318 to 1350 cm^{-1}, depending on the anion. In $Co(NH_3)_6Cl_2$ it is observed at 1163 cm^{-1}.[41] While this band is not the most sensitive to oxidation state change in the metal ammines, it is fairly sharp and usually well separated from other bands in these complexes. In the preparations reported in the earlier work, the band at 1172 cm^{-1} was between 20 and 35% of the total intensity of the band at 1292 cm^{-1}.[40] This means, if the assignment is correct, there is approximatel y that much impurity hexaammine in the sample since the intensities of this band in both

Co(II) and Co(III) complexes are the same. Since this much strongly paramagnetic Co(II) should be easily detected in the presence of the Co(III) compound, this assignment of structures should be easily tested. In all of these studies, an important point had been neglected. No study ever reported complete analytical data on the compounds used. And no one had analyzed for NO, either directly or by, for example, a total nitrogen!

Several preparations were obtained, and the infrared spectra of products were compared with the reported spectrum. We obtained the identical spectrum as observed by Mercer, et al., with one tiny additional band at 1400 cm^{-1}. (We will discuss the 1400 cm^{-1} band later.) Varying the ammonium hydroxide concentrations, temperature, and time of reaction had no effect on the intensity ratio of the 1291 cm^{-1} to 1172 cm^{-1} bands. While Mercer, et al., claimed to have recrystallized the black isomer, we were never able to reproduce this step. Others have made this observation about Mercer's work.[42]

Microscopic examination of these crystals showed uniform black bipyramids with no evidence for as much as 5% $Co(NH_3)_6Cl_2$. The magnetic susceptibility determination on several preparations gave χ_M' (298 °K) values of approximately $+350 \times 10^{-6}$ cgs units. This susceptibility increased by about a factor of two down to 77°K. Although the 298°K value is somewhat high for a Co(III) T.I.P. term, it is small compared to a value of $+6,250 \times 10^{-6}$ expected for a Co(II) salt. The room temperature susceptibility and temperature dependence are consistent with approximately two parts in one hundred Co(II) impurity in a Co(III) salt, but no greater amount of that impurity.

An analysis of a sample of this compound was then performed. Cobalt was determined by first dissolving a weighed sample of the black salt in a dilute HCl solution. This decomposes the compound into Co(II) hexaquo ion, NH_4^+ ion and the NO was swept out with an Ar purge. The cobalt was then determined by a standard method with ferricyanide which was standardized with primary standard KIO_3.[43] Cobalt was also determined by an outside laboratory analysis.[44] Chloride was determined by the outside laboratory.[44] The nitrosyl to cobalt ratio was determined by weighing into a small flask a sample of the black salt and excess solid oxalic acid. This flask was then evacuated to less than 10^{-3} torr total pressure. The flask was then immersed in liquid nitrogen and degassed water distilled into this flask. The flask was then closed off from the vacuum system and allowed to warm up to room temperature. The oxalic acid solution then decomposed the black salt, giving off the NO. The evolved gases were then passed through a dry-ice-acetone trap (using a toepler pump) and the pressure and volume of the gas measured. A sample of this gas was then submitted for mass spectroscopic analysis. Ammonia was determined by several methods. The actual determination was made by titrating the evolved NH_3 as ammonium borate with standard sulfamic acid, using methyl red indicator.[45] The ammonia was driven off the complex by two methods. One method was to drop a weighed sample of the compound into an Ar flushed concentrated (5 M) NaOH solution, and then distill the ammonia into the boric acid solution. The other method is considerably more elaborate.

A DuPont thermogravimetric analyzer, as modified by Kerr,[46] is used to heat a weighed portion of the sample in flowing nitrogen. The ammonia in the effluent gas is determined continuously.

This experiment shows three distinct materials are formed in going from $[Co(NH_3)_5NO]Cl_2$ to $CoCl_2$. The composition of each phase can be calculated from the mass loss and the ammonia determination. The NO can be found by difference from these data. Infrared spectrum of each intermediate compound was obtained.

The results of all these determinations are given as both percentages compared to theoretical, ratios of analyzed species, and by the total of all analyzed species.

%Co; found, 24.69%, theot. 24.06%

%Cl; found, 28.49%, theot. 28.95%

%NH_3; found 34.20%, theot. 34.45%

%NO; found 12.15%; theot. 12.25%

NO was found 99+% pure by mass spectrometry.

$$\frac{NO}{Co} = 0.99 \qquad \frac{NH_3}{Co} = 4.95 \qquad \frac{Cl}{Co} = 1.99$$

Total; 99.53%

Based on these data, there is less than 1% impurity in the preparation.

The thermogravimetric data give these intermediate compositions:

$$[Co(NH_3)_5NO]Cl_2 \xrightarrow{90 \text{ to } 175\,^{\circ}C} Co(NH_3)_2Cl_2 + 3NH_3 + NO$$

NH_3; found 2.91 mg; theot. 2.19 mg

NO; by difference, found, 1.20 mg; theot. 1.26 mg

$$Co(NH_3)_2Cl_2 \xrightarrow{180 \text{ to } 225\,^\circ C} Co(NH_3)Cl_2 + NH_3$$

NH_3; found 0.90 mg, theot. 0.92 mg, total weight change 0.92 mg

$$Co(NH_3)Cl_2 \xrightarrow{230 \text{ to } 290\,^\circ C} CoCl_2 + NH_3$$

NH_3; found 0.92 mg, theot. 0.92 mg, total weight change 0.92 mg.

These intermediates are observed in the thermal decomposition of $Co(NH_3)_6Cl_2$.[47] The first step in the hexaammine involves the loss of $4NH_3$, where we see $3NH_3$ plus NO. Otherwise the thermograms are identical. The thermogravimetric analyses are determined at a 5 °C heating rate in nitrogen flowing at 150 $cm^3\ min^{-1}$. The actual sample sizes vary to obtain optimum analytical data, but in each case the total NH_3 determined was within 2% of theoretical total, and the final weight of $CoCl_2$ was within 1% of the weight calculated from initial weight.

There was a significant change in the infrared spectrum after the first step in the decomposition. The 1600 cm^{-1} band in the starting compound decreased markedly in intensity. This was due to the loss of NO which overlaps the normally weak band due to the δ_d motion of the coordinated NH_3. The 1172 cm^{-1} band completely disappears.

The 1172 cm^{-1} band must be due to the NH_3 group coordinated trans to nitrosyl in the compound, $[Co(NH_3)_5NO]Cl_2$. This is confirmed by examining the crystal structure determination results.[26] The cobalt-nitrogen bond distances for the four ammonias cis to the nitrosyl are all 1.98Å, approximately that found in $Co(NH_3)_6I_3$; 1.94Å.[48] The Co-N distance for the nitrogen trans to the nitrosyl is found as 2.22Å, slightly longer than the distance 2.11Å found in $Co(NH_3)_6Cl_2$.[48]

The bond at 1172 cm^{-1} is not due to an impurity but rather as a result of the large trans effect of the NO^- ligand.

The small band at 1400 cm^{-1} is due to an impurity. Its intensity varies from preparation to preparation. This band does not change on preparing the deuterated compound. We have not been able to identify this impurity. There is one infrared spectrum reported which could account for this impurity band. This spectrum is found as spectrum Y 289 K in the Sadtler Research Laboratories catalog of infrared spectra. The compound is said to be $[Co(NH_3)_5H_2O]Cl_2$ from G. F. Smith Chemical Co. We can find no other mention of this compound in the literature, and the company does not list the compound in the current catalog. The spectrum is not the one expected for that compound. Since the impurity is very small we have not pursued this identification.

Confident of the preparative method and of our methods of characterizing the product of the preparations, we attempted preparations to check on the yield of monomer as a function of time temperature, and anion. These results are summarized in the following table.

	Time of	Yield of Monomer at Temp.	
Anion	Reaction	0 °C	25 °C
Cl^-	15 min	90%	75%
	3 hrs	50%	25%
NO_3^-	15 min	50%	0%
	3 hrs	30%	0%
Acetate	up to 3 hrs	0	0

The initial cobalt(II) concentration was 0.15 M. The $NH_3 \cdot H_2O$ concentration is approximately 7 M. The preparation with the Cl^- anion after 15 min had considerable impurity in it as judged by the intensity of the 1400 cm^{-1} band. No insoluble product was obtained with the acetate anion. These data will be useful later in discussing the formation of the red dimer.

Now consider a study of the equilibrium:

$$[Co^{II}(NH_3)_5X]^{+2} + NO \rightleftharpoons [Co^{III}(NH_3)_5NO]^{2+} + X$$

where X is NH_3, H_2O or OH^-.

The starting complex is written as it is because the state of this ion is not known. The formation constants for cobalt(II) ammines are much smaller than for Co(III) ammines.[49] From these constants we can calculate that, if the NH_3 concentration is 7 M, and the starting Co(II) concentration is 0.12 M, the distribution of species is approximately:

44% $Co(NH_3)_6^{+2}$

45% $Co(NH_3)_5^{+2}$, other ligand unknown, probably H_2O.

8% $Co(NH_3)_4^{+2}$, other ligands unknown.

3% cobalt with less than 4 ammine ligands.

In principle, we can study the above equilibrium by varying the pressure of NO over the solution and analyze for the relative amounts of cobalt nitrosyl to total cobalt. As an experimental problem this is somewhat more difficult. Analyzing the solution phase would be complicated by the several non-nitrosyl species, and the fact that the nitrosyl solutions are very intensely colored. The solution spectrum of the nitrosyl monomer is not known, and as we will see later, might not be easily measured.

We decided to use the following method. The equilibrium would be determined in a constant volume apparatus where we could measure the total pressure of the gases over the liquid (H_2O, NH_3, NO). If we know the volume of the apparatus, we can obtain the number of millimoles of NO that appear in the gas phase, or disappear into the solution phase. If we know the number of millimoles of cobalt in the solution, we can obtain the ratio NO/Co in the solution and, hopefully, the ratio of nitrosyl to non-nitrosyl complex.

The apparatus consisted of two bulbs of 500 ml and 1000 ml capacity (approximately) connected by a stopcock, with the larger bulb also connected to a standard vacuum line. The smaller bulb was surrounded by a jacket for variable temperature measurements. A pressure transducer was attached to the large bulb.[50] The pressure transducer was calibrated using known volumes and pressures measured with a mercury manometer. The voltage across the transducer was adjusted to give an output signal of approximately 1 mV per torr. The device was linear in voltage output vs. pressure in the range 0-1500 torr with a sensitivity of 1.013 mV $torr^{-1}$. The accuracy of the transducer is such that pressure measurements have an uncertainty of ± 2 torr.

The typical experiment was to place a solution in the smaller flask, degas the solution several times, and then close off the connecting stopcock. The large bulb was then filled to the desired pressure and closed off. The connecting stopcock was then opened and the pressure change recorded as a function of time. There will be an instantaneous pressure change due to the expansion of gas from the bulb initially at the higher pressure to the entire system. This can be calculated from the ideal gas law. To obtain agreement between calculated and observed pressure changes an additional assumption needs to be made. This is that there is no counter diffusion of gases through the small stopcock bore. This is an unfortunate occurrence, but not unexpected. However, good agreement between calculated and observed pressure changes was obtained with this assumption, and the error in this assumption was found to be, experimentally, less than 4 torr in six hours, a negligable error for this work.

Using this apparatus and various solutions, we made the following initial observations:

1. The solubility of NO in ammonium hydroxide solutions up to 1000 torr is not detectably different from the solubility in water, which is very small; 4 cm^3 of gas at S.T.P. in 100 ml of H_2O at 30°C.[51]

2. The equilibrium vapor pressure of NH_3 over the cobalt-ammine solutions does not change significantly until after at least six degassing cycles, as expected when calculated from the volume of the apparatus and the known solubility of NH_3 in H_2O.[52]

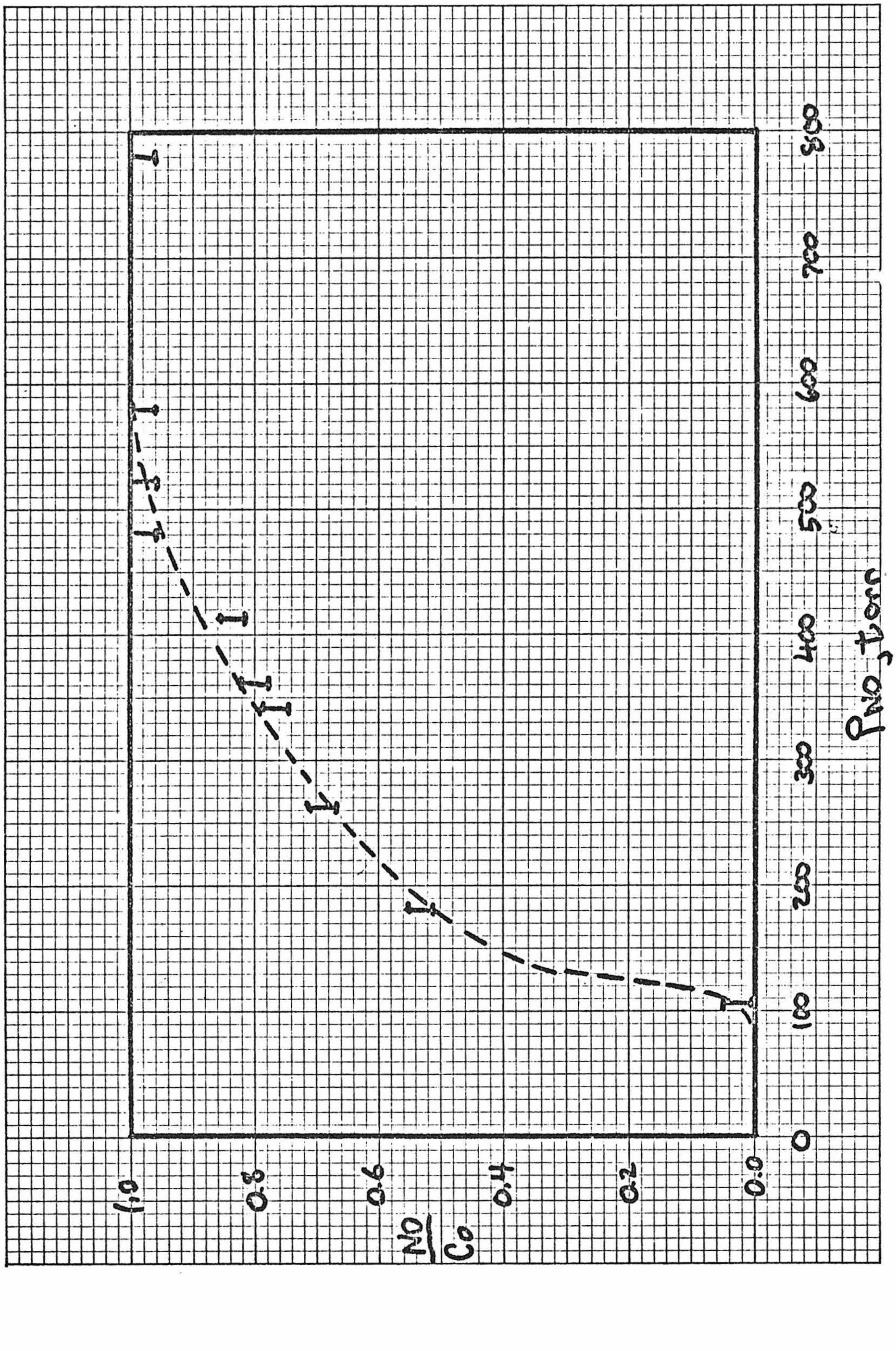
3. The absorption of NO by ammoniacal Co(II) solutions appears to be limited by the rate of diffusion through the liquid for this apparatus. However, the NO uptake was about 95% complete with respect to the theoretical values of 1 NO per Co at high pressures within 15 minutes.

4. The reaction with NO is reversible at low pressures, and at higher pressures is almost reversible. It may be completely reversible except for the time needed to reach equilibrium in this apparatus. If the NO pressure is high enough to obtain a ratio of NO to Co of 0.95 and we pump off the NO and repeat the experiment, about 20% of cobalt is unreactive in the second cycle.

We then proceeded to determine the ratio of NO to Cobalt in solution as a function of the pressure of NO over the solution. This was done with acetate anions at 0.15 M cobalt concentration so no solid phase is observed. This gave the points on the right-hand portion of Figure 1. We could not make measurements at lower final pressures of NO in our apparatus. However, we knew that if we tried to dissolve the chloride salt in an ammonia solution, it would decompose almost completely. This means this curve has a sharp sigmoid shape.

We confirmed the point at p_{NO} of about 100 torr by dissolving a known amount of $[Co(NH_3)_5NO]Cl_2$ in an ammonia solution in a separate experiment. A small bulb was attached to a vacuum line also containing a mercury manometer. This bulb contained an ammonium hydroxide solution which was purged with N_2 to remove any oxygen. This solution was frozen with liquid nitrogen and then the bulb was evacuated, and then the bulb closed off from the pump. The bulb and solution was then warmed up to 25 °C and the pressure recorded. The solution was then refrozen in liquid nitrogen and the bulb opened under a nitrogen atmosphere. A weighed sample of $[Co(NH_3)_5NO]Cl_2$ was added to the bulb. This sample was of such size to give a cobalt concentration of about 0.2 M in the resulting solution, and if completely decomposed, would have 100 torr NO pressure over it. The bulb was then evacuated again and so on. The pressure rise was again noted. It exceeded the previous pressure rise by 105 torr, that is, the complex completely dissociated. This provided the point on Figure 1 at 100 torr.

Figure 1. NO to cobalt ratio as a function of NO pressure.



1.0
0.8
0.6
0.4
0.2
0.0
NO/Co
0
100
200
300
400
500
600
700
800
P_NO, Torr

The equilibrium constant was also estimated at 40 °C by making one measurement with the solution at that temperature. The final pressure of NO was 360 torr, and the ratio of NO to cobalt in solution was 0.80, so we conclude the equilibrium is only slightly less favored at 40 °C.

The equilibrium constant was also determined with a cobalt acetate solution with the cobalt concentration 0.40 M. Here the final pressure of NO was also 360 torr and we found the same ratio of NO to cobalt, 0.80. The equilibrium was determined using a cobalt nitrate solution at a final pressure of 470 torr NO. Here the ratio of NO to cobalt was 1.0, so the nitrate anion is not a factor in this equilibrium.

This behavior is not that expected for a simple equilibrium as written above. The curve is not described by any simple integral exponent power of p_{NO} either. The solution does not take up more than one NO per cobalt at higher pressures, and we can rapidly separate a monomeric nitrosyl from the solution if Cl^- anions are present. We therefore think species with more than one NO per cobalt are not likely. If the Co(II) solution contained a good fraction of the cobalt ions bound in polynuclear species, and these species reacted to break apart and give more reactive cobalt moieties, we might explain the observed behavior. This would be, in principle, similar to the observed uptake of O_2 in hemoglobin where the binding of the first O_2 makes binding of additional O_2 easier. The evidence is that polynuclear Co(II) ions do not exist in these solutions, however. The equilibrium constants for the stepwise addition of ammonia to cobalt(II) ammines fall smoothly as the number of ammines increase.[53] This suggests the entropies and enthalpies of these reactions are characteristic of monomeric species and not of more complex polynuclear ions.[53] If we look at the methods of synthesizing polynuclear Co(III) ammines, we see these are not made from amide-bridged cobalt(II) species, but from O_2^- bridged or $O_2^=$ bridged Co(II), Co(III) ions formed when the Co(II) solutions are exposed to oxygen.[54]

Using the reaction between O_2 and Co(II) ammines as a model, we might consider parallel reaction when NO is used instead of O_2. There are reports of a rapid, reversible oxygenation of Co(II) ammines, which then react slowly to make the binuclear Co(III) ammines bridged by oxygen species.[55,56,57] The equilibrium reaction has been studied in very dilute solution by Simplicio and Wilkins.[58] They show the reaction is mainly from the aquopentamminecobalt(II) and have determined the equilibrium constant for the reaction:

$$2Co(NH_3)_5(H_2O)^{2+} + O_2 \rightleftharpoons [(NH_3)_5CoO_2Co(NH_3)_5]^{4+} + 2H_2O$$

is on the order of 3×10^6. They also have provided data on the rates of the forward and reverse reactions. The ratio of O_2 to cobalt is only one-half in this reaction so it is not an exact parallel of the nitrosyl reaction.

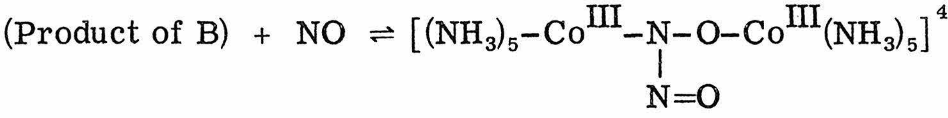
There are two possibilities that we can suggest at this point.

1. The NO reacts with a Co(II) complex to form a monomeric nitrosyl. This reacts with another Co(II) monomer to produce a dimeric ion, similar to the O_2 bridging group above. This reacts

rapidly with another NO to make the ion shown at the end of the scheme:

$$\text{Co(II) ammine} + \text{NO} \rightleftharpoons [\text{Co}^{\text{III}}(\text{NH}_3)_5\text{NO}^-]^{2+} \qquad \text{(A)}$$

$$\text{(Product of A)} + \text{Co(II) ammine} \rightleftharpoons [(\text{NH}_3)_5\text{Co}^{\text{III}} \leftarrow \text{N–O} \rightarrow \text{Co}^{\text{III}}(\text{NH}_3)_5]^{4+} \qquad \text{(B)}$$

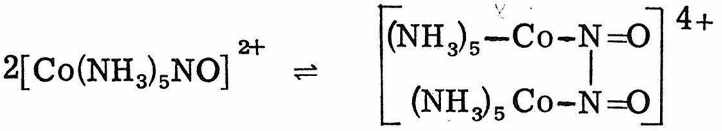


$$\text{(Product of B)} + \text{NO} \rightleftharpoons [(\text{NH}_3)_5\text{–Co}^{\text{III}}\text{–}\underset{\substack{|\\ \text{N=O}}}{\text{N}}\text{–O–Co}^{\text{III}}(\text{NH}_3)_5]^{4+} \qquad \text{(C)}$$

This product might be unstable and will then slowly (typical Co(III) rate) rearrange to give at least some of the dimer product observed after much longer times. The first equilibrium might not be too favorable, but once the monomer concentration becomes large, the rest of the reactions become important.

2. The other possibility results from the observation that in other reactions were NO^- is produced, it always dimerizes to $N_2O_2^{=}$. This leads to this scheme:

$$\text{Co(II) ammine} + \text{NO} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{NO}]^{2+} \qquad \text{(A)}$$



$$2[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+} \rightleftharpoons \left[\begin{array}{c}(\text{NH}_3)_5\text{–Co–N=O}\\ | \\ (\text{NH}_3)_5\,\text{Co–N=O}\end{array}\right]^{4+} \qquad \text{(D)}$$

This product is unstable because of the crowding of the $(NH_3)_5Co(III)$ groups. This also will rearrange to give the product dimer observed.

In both of these reactions the overall scheme is of the sort:

$$2\ \text{Co(II) ammines} + 2\,\text{NO} \rightleftharpoons [\text{dimeric ion as above}]$$

which could account for an exponent greater than one for the p_{NO} dependence.

To express the p_{NO} dependence of the ratio NO to cobalt in a closed form for these schemes is a difficult problem. Without more information as to the shape of the curve and to the NH_3 pressure and OH^- ion concentration dependence of the observables in this experiment there seems to be little point in trying to develop an expression for this purpose.

We favor the second scheme for several reasons. The reversability of this reaction appears more likely. In the first scheme, once the second NO is attached and the electron transfer occurs, there seems to be no driving force to decompose that ion and allow the reactions to be reversible. In the second scheme the steric crowding would considerably weaken the N-N bond. The second scheme occurs in one step past the monomer, whereas in the first scheme several steps are needed. However, it does not seem possible to decide between these possibilities at this point.

This represents the end of the work on this aspect of the chemistry of this reaction. We would have liked to study the above reactions in greater detail since this looks like a promising direction. In planning this study, however, we estimated the analytical problems in separating the various Co(III) species after the reactions that follow the formation of the monomer would be the experimentally difficult part of this study. While these problems were difficult (and not all solved, as will be seen), it is clear the above system will not be trivial to sort out. Unfortunately, we examined this reaction only near the end of the study and could not obtain more data. We now have a much better idea where the interesting reactions occur in this system. That is some kind of progress.

The Red Isomer

The conditions of synthesis of the red isomer were the first problem encountered in the study of this isomer. The literature reports of success are all with nitrate as the anion.[25,28,34,39,40] (There is one report of the sulphate salt, but this is very suspect since the major product of the reaction is aquopentaamminecobalt(II), and the sulphate of this ion is not very soluble.)[34] We attempted the synthesis of the red isomer at various ammonia and cobalt(II) concentrations with the anions Cl^-, NO_3^-, and acetate. The black isomer has also been obtained as the sulphate, thiocyanate, and iodate, but we did not try to make the red isomer of these anions.[28,33]

Air, or at least, oxygen, must be excluded from the reaction to produce the red isomer pure. In the presence of air, dimeric oxo-bridged Co^{III} complexes are found as impurities in the solid products. The presence of air is easily detected upon passing NO gas through the ammonium hydroxide solution. Some of the NO is oxidized to NO_2, and the mixture of NO, NO_2, H_2O, and NH_3 react to make ammonium nitrite:

$$NO + NO_2 + H_2O + 2NH_3 \rightarrow 2NH_4NO_2$$

and ammonium nitrate:

$$3NO_2 + H_2O + 2NH_3 \rightarrow 2NH_4NO_3 + NO.$$

These salts form a dense white smoke over the solution. The presence of this white smoke is a quite sensitive test for oxygen in the apparatus.

Nitric oxide does not react with solutions of cobalt(II) in ammonia if the pH is less than about 9. We could not obtain any red isomer if the ammonium hydroxide concentration exceeded about 10M (conc. NH_4OH is sold as approximately 15M). The black isomer forms in concentrated ammonia, but is contaminated with $Co(NH_3)_6^{2+}$ compounds.[38] Even with nitrate anions, no hyponitrito-bridged dimer precipitated from these solutions.

The cobalt concentration was varied from 0.10M to 0.45 M. Concentrations of Co(II) higher than 0.45 M in solutions that were 7M in ammonium hydroxide caused precipitation of a light pink colored solid phase. The composition of this solid material was not determined.

Within the field of ammonia and cobalt concentrations given above, the effect of various anions on the yield of red isomer was investigated. If the anion is chloride, the precipitation of the monomeric black isomer occurs and essentially stops the reaction at that point. Slow hydrolysis of the monomer to give $[Co(NH_3)_5OH]^{2+}$ does occur but relative to the other anions discussed below the reactions stop with the precipitation of the monomer.

If the anion is acetate, no insoluble products are seen for the entire range of cobalt concentration. For the more dilute solutions, no red isomer is found after 3 hours. Solutions originally 0.4M in cobalt(II) acetate do precipitate red isomer if excess nitrate is added after three to four hours. The yield of red isomer is about 10%. The solid was found to be identical to that obtained from preparations starting with nitrate anions by infrared spectroscopy. While the yield is low compared to the yields obtained with nitrate (we will discuss this point later), this indicates nitrate is not necessary for the formation of the hyponitrito bridge. If the anion was nitrate and the cobalt concentration 0.40 to 0.45M, yields of 20 to 25% red isomer were obtained, based on Co(II). If the cobalt concentration was 0.15M or less, no solid product was obtained. Measurements of the solubility of the red isomer as the nitrate salt in ammonium hydroxide solutions show that the solid will precipitate if the concentration of the cobalt(III) (which is twice the concentration of the "red" ion) is greater than 0.05M. This means that if 25% of the original 0.15M cobalt solution were converted to the red isomer, no solid would precipitate. However, addition of a large excess of nitrate (as KNO_3) did not precipitate any solid, and infrared spectra obtained on the solid obtained by precipitating all of the cobalt containing species (as described later) showed no red isomer was present in this solution.

The solubility of the red isomer was determined in ammonium hydroxide solutions of 2M, 5M, and 7M concentration. The solubility did not change with ammonium hydroxide concentration. The determination of the solubility was made by measuring the intensity of the 20,000 cm^{-1} transition, $^1T_{1g} \leftarrow {}^1A_{1g}$ (seen in most Co(III) complexes) spectrophotometrically with a known concentration of red isomer. Then solutions in contact with solid were examined as a function of time until the intensity of the absorbtion band was constant within a few percent. In well stirred solutions equilibrium was obtained within fifteen minutes. The compound does hydrolyze at a slow rate in these ammonium hydroxide solutions, but in 2M ammonium hydroxide there was no detectable hydrolysis in the time needed for this measurement.

The other products of the reaction were identified by infrared spectroscopy. All of the cobalt containing species could be precipitated by the addition of anhydrous (denatured) ethanol to the reaction mixture after neutralizing the ammonium hydroxide, usually with nitric acid. In the unbuffered solutions used for these original studies, the solution phase was clear and colorless after the solids were filtered off. The infrared spectrum of the solid phase showed $[Co(NH_3)_5H_2O](NO_3)_3$ was the major product. Smaller amounts of $[Co(NH_3)_5NO_2]^{2+}$, $[Co(NH_3)_5ONO]^{2+}$, and $[Co(NH_3)_5NO_3]^{2+}$ were seen in the solid, depending on the length of time between starting the reaction and precipitating the solid.

The red isomer, μ-hyponitritobis[pentaamminecobalt(III)] nitrate was identified by its infrared spectrum and chemical analysis.[40] For $[CoNO(NH_3)_5]_2(NO_3)_4$; Co, 19.77%; found, 20.09%.[44] The other cobalt complexes were identified by comparisons of the unknown spectra with literature infrared spectra or with spectra obtained on samples prepared by well-known methods.[41] Because of the mixture of Co(III) products obtained, it was not possible to use visible-U. V. spectroscopy for either the ligand field or charge-transfer positions of the spectrum to analyze the solution phase for the relative amounts of these species. Attempts to selectively precipitate the 4+ cation of the red isomer from solutions containing large amounts of $[Co(NH_3)_5H_2O]^{3+}$ or $[Co(NH_3)_5OH]^{2+}$ were unsuccessful with any anion except nitrate. Ion exchange chromotography was attempted, but poor results were obtained. The elutions were too slow and some hydrolysis of various ions caused poor separations. Polarographic analysis with a dropping mercury electrode was attempted as a possible method for analyzing the solution for the various ions present. In principle this method could be used, but problems encountered in suppressing maxima in the various waves prevented a straightforward application.

The preliminary study was completed with a determination of the yield of the red isomer as a function of temperature. 0.40M Co(II) nitrate in 7M ammonium hydroxide solution was saturated with NO at -8°, 0°, -15°, 25°, and 40°C. At the end of four hours any solid present was filtered off, washed with ethanol, dried overnight in a vacuum desiccator over P_2O_5 and then weighed. The infrared spectrum was obtained on a portion of the solid. Only at 25° was a pure sample of the red isomer obtained, in 20% yield. At -8° and 0°, the solid was the monomeric black isomer in low yield. At 15°C, approximately half the solid was red isomer (estimated yield 10%) the rest of the solid was $[Co(NH_3)_5NO_2](NO_3)_2$. At 40 °C only a very small amount of solid was obtained, and it proved to be a mixture of $[Co(NH_3)_5ONO]$-$(NO_3)_2$ and $[Co(NH_3)_5NO_2](NO_3)_2$ by infrared determination.

At this point we had run out of obvious things to try, so we decided to study some kinetics. But we could not analyze the rate of production of cobalt(III) products because we could not separate the various complexes quickly and conveniently. However, there was an interesting possibility to use the reversibility of formation of the monomer to determine the rate of disappearance of the monomer. At this point in time, we simply assumed that the black solution formed initially contained only monomeric $[Co(NH_3)_5NO]^{2+}$. We thought that if we started with 0.15M Co(II), the monomer formed and was hydrolyzed in base:

$$[Co(NH_3)_5NO]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + NO^- \qquad (A)$$

and the NO^- reacted further as suggested by Gans:

$$NO^- + 2NO \rightarrow N_2O + NO_2^-. \qquad (B)$$

We knew from earlier experiments on the black isomer that if we extracted an aliquot from the above reaction (A) and put it into a solution containing ammonium hydroxide and $Fe(CN)_6^{3-}$, the $[Co(NH_3)_5NO]^{2+}$ ion decomposed and reacted as a Co(II) compound, whereas the $[Co(NH_3)_5OH]^{2+}$ did not react. The NO^- acted as the reductant and left the ion as NO. Using this reaction, we proceeded to measure the disappearance of Co(II), and hence the rate of hydrolysis, of the first formed cobalt ammine nitrosyl complex.

Since base hydrolysis of cobalt complexes are usually dependent on hydroxide ion concentration, we prepared a buffer solution of 4M ammonium acetate in 4M ammonium hydroxide.[59] The pH of this solution was measured as 10 with a glass electrode. The calculated pH for this buffer system at dilute concentrations is 9.25.[50] The agreement is actually quite good for such a concentrated solution. We used this buffer for all the kinetic measurements reported here. Attempts to prepare solutions buffered at different pH values all failed to hold the pH within ±0.5 pH unit in the course of the reaction. We simply assume the reaction we are following is the usual second order hydrolysis but were not able to demonstrate the dependence of the rate on hydroxide ion concentration.

The typical kinetic experiment was run starting with 0.15M Co(II) concentration in the ammonia-ammonium acetate buffer. The reaction vessel was immersed in a two liter beaker filled with room temperature water to serve as a constant temperature bath. The temperature never varied more than ± 0.2 °C for any particular kinetic run. Time zero was taken as the moment the vigorous NO purge was turned on, the solution having been previously deoxygenated with argon or nitrogen. Aliquots of 5.0 ml were removed using an argon purged syringe and discharged into a prepared excess of the $Fe(CN)_6^{3-}$ ammonia solution. Aliquots were removed as often as once every ten minutes for some runs. All of the runs were made between 22 °C and 23 °C.

The results of a typical run are given in Figure 2. For the first approximately 40 minutes, very little reaction which removes the "easily reduced to Co(II)" species is detected. After this induction period, the Co(II) concentration drops smoothly. Figure 3 shows a first order plot, that is, log concentration vs. time, for the Co(II) concentration from 50 minutes to 270 minutes. It appears to be a good straight line. If we assume the reaction is pseudo first order because of the constant value of OH^- concentration, we obtain a first-order rate constant. If we then use the known OH^- concentration, we obtain a second order rate constant for the hydrolysis of 0.61 $sec^{-1}M^{-1}$ for this reaction. This rate constant is about the same value as observed for the hydrolysis of $Co(NH_3)_5Cl^{2+}$.[59]

We then attempted to extend the rate of disappearance studies to more concentrated Co(II) solutions. Here we ran into analytical problems. The addition of the aliquot containing the Co(II) and Co(III) species to the $Fe(CN)_6^{3-}$ solutions caused precipitation of unknown solids, and non-reproducible results for the determination of Co(II) were observed.

The experiments attempted so far raised as many questions as they provided answers. Two questions raised by the kinetics study were pursued farther. The forty or fifty minutes between admitting NO and the beginning of the reaction consuming the reversibly formed complex needed more attention. Also, the identification of the products of the hydrolysis reaction appeared to be a worthwhile effort.

Figure 2. Cobalt(II) concentration as a function of time.

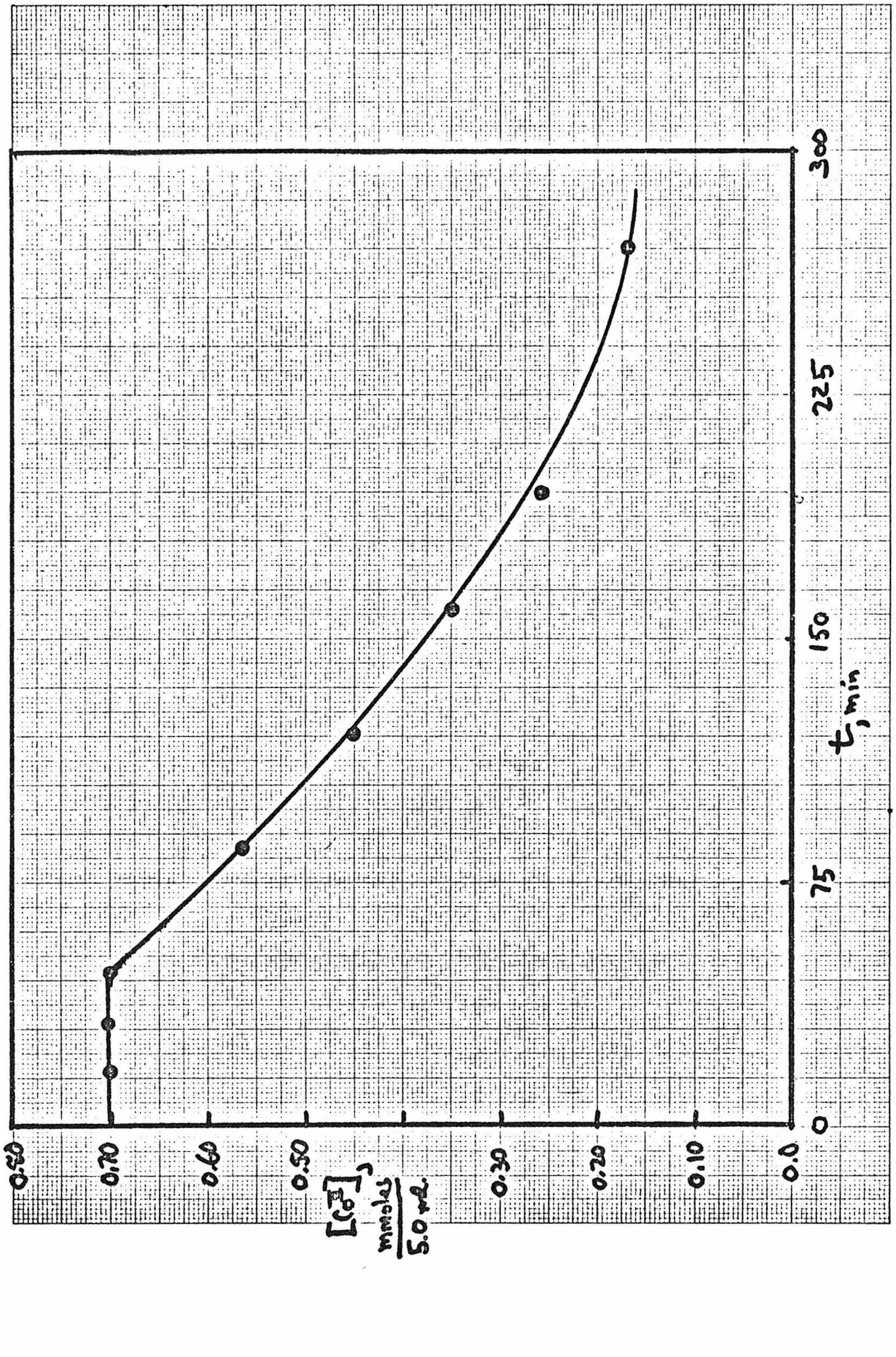
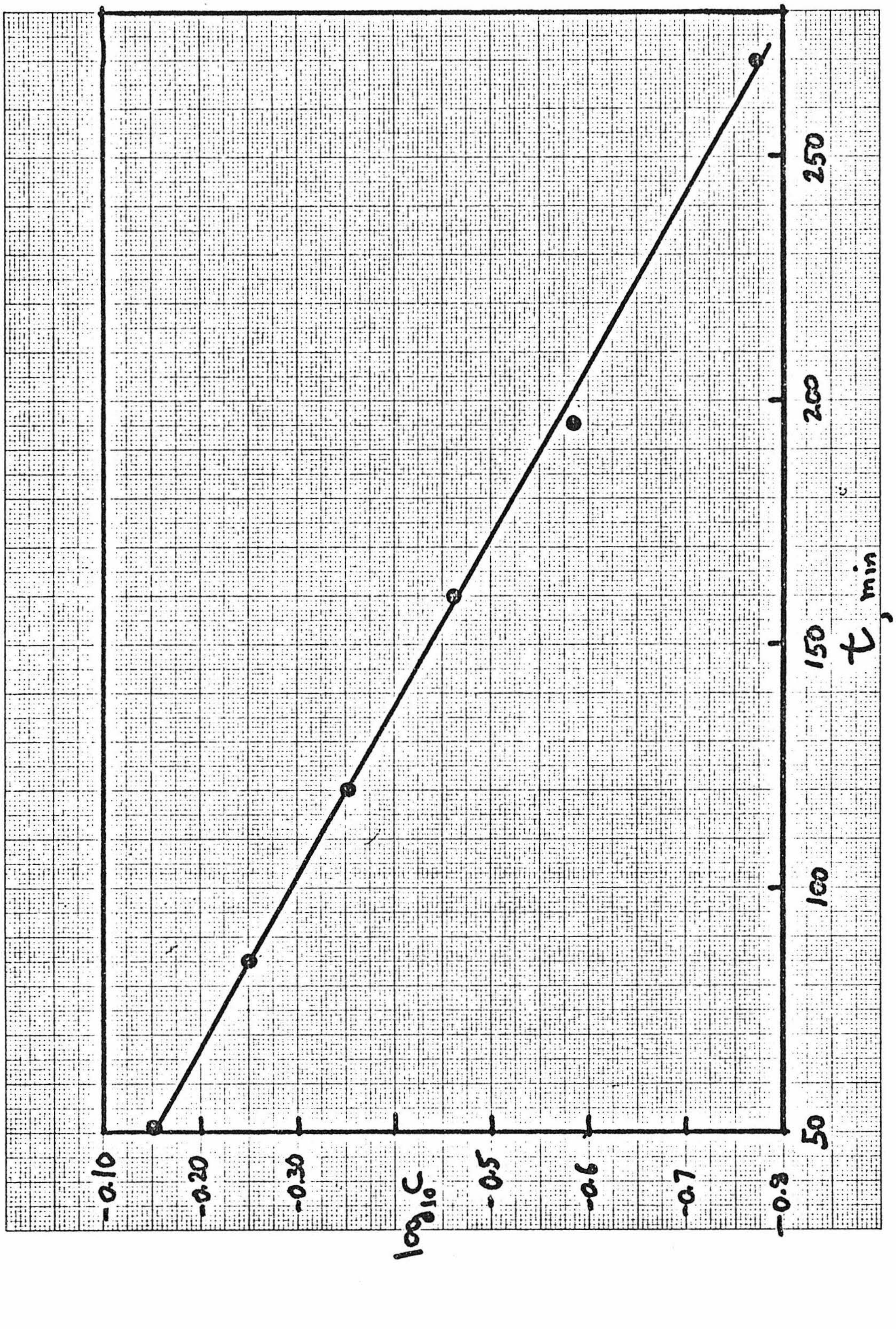

$[Co^{II}]$, $\frac{\text{mmoles}}{5.0\ \text{ml}}$
0.80
0.70
0.60
0.50
0.30
0.20
0.10
0.0
0
75
150
225
300
t, min

Figure 3. Log of cobalt concentration vs. time showing first order kinetics.


-0.10
-0.20
-0.30
$\log_{10} C$
-0.5
-0.6
-0.7
-0.8
50
100
150
200
250
t, min

The study of the first forty minutes is discussed in the earlier chapter on the black isomer. Although we cannot be completely sure at this time, it appears that the induction period is a result of the poor mixing of the gas and liquid phases in the original kinetic experiments.

The identification of the overall stoichiometry of the reaction with dilute Co(II) concentrations was done in the fixed volume apparatus used for studying the initial reaction of NO with the Co(II) solutions. After the initial pressure drop corresponding to one NO per Co, the mixture was stirred for six hours and the total pressure monitored. This experiment was done at 25 °C, once with nitrate and once with acetate anions. The total pressure change for both reactions was the same. After the six hour period the gas in the bulb over the solution was condensed into a separate trap and closed off from the system. This gas sample was analyzed by infrared spectroscopy on a portion collected in a gas cell at a pressure of 100 torr. For both anions, the spectra were identical. For the nitrate anion the gas mixture was analyzed by fractionally distilling the mixture through cold traps. The volume of each gas was measured at a known pressure, and the composition of each sample checked by its infrared spectrum. The gas phase contained H_2O, NH_3, N_2O, and NO vapor. The entire mixture was condensed in liquid nitrogen. The trap was then placed on a vacuum line which consisted of several additional traps and a toepler pump for moving gases through the line. The trap containing the mixed gases was attached to the line and the line was evacuated and closed off. The mixed gases were then warmed up to -78 °C with a Dry Ice-acetone mixture. The NH_3 was collected in a trap maintained at -130 °C by a pentane slush bath. The N_2O was collected in a trap at -183 °C using liquid oxygen. The NO was pumped through all of these traps. The N_2O was contaminated with some NH_3, but the composition of the N_2O, NH_3 mixture was estimated from the intensities of the infrared bands of ammonia.[60]

The solution phase was also analyzed. The amount of Co(II) left unreacted was determined. NO_2^- was analyzed for by adding NaOH and heating the solution to expel all the ammonia. The Co_3O_4 was filtered off and the solution neutralized with sulfuric acid. The solution was then mixed with excess Ce^{IV} in $2NH_2SO_4$ and the nitrite oxidized to nitrate:

$$NO_2^- + Ce^{IV} + H_2O \rightarrow NO_3^- + Ce^{3+} + 2H^+$$

The excess Ce^{IV} is then determined with Fe^{2+} by a standard potentiometric titration.[61] However, if the solution contains hyponitrite, this would interfere with the determination of nitrite by this method.[62] This analysis was not completely satisfactory. The nitrite analysis was high, as would be expected. Using a mass and charge balance on the number of electrons provided by the Co(II) to Co(III) oxidation, the total pressure change and the gas phase composition, we could complete the analysis.

The overall reaction was found to be:

$$\mathrm{Co(II)} + 3\mathrm{NO} \rightarrow \mathrm{Co^{III}} + \mathrm{N_2O} + \mathrm{NO_2^-}$$

The solution absorbs one nitric oxide per cobalt(II) initially. After this reaction the total pressure drops very slowly for the next five hours. The pressure drop is quite slow over this entire priod and corresponds to one additional NO per cobalt that is oxidized to Co(III). Since the composition of the gas phase is changing over this period the kinetics of the slower reactions may not correspond to the total pressure change. Therefore we have not tried to extract any additional details out of this data.

Since the reaction:

$$2\mathrm{OH^-} + 2\mathrm{NO} + \mathrm{NO_3^-} \rightarrow 3\mathrm{NO_2^-} + \mathrm{H_2O}$$

has a standard potential of +0.45 V in base, we determined if this reaction occurred at a significant rate in a solution of $NaNO_3$ in ammonium hydroxide at 25 °C.[63] We found no evidence for reaction at 800 torr NO pressure after eight hours.

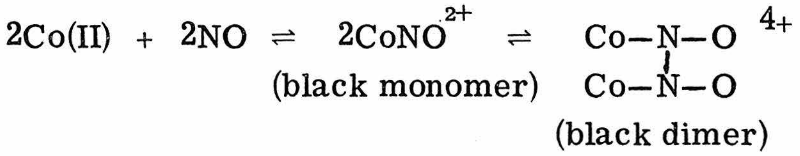
Summary and Observations

We are now in a position to dispute the previously proposed mechanism explaining the reaction of nitric oxide with ammoniacal cobalt(II) solutions. If we can do this, we are also given the honor of proposing another mechanism to replace the demolished one.

If the nitric oxide pressure is at least one atmosphere over the solution phase, then the reaction:

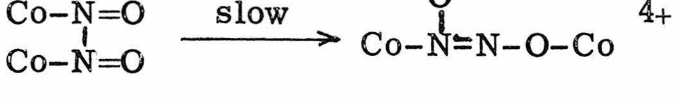
$$[(NH_3)_5CoH_2O]^{2+} + NO \rightleftharpoons [(NH_3)_5CoNO]^{2+} + H_2O$$

goes essentially 100% to the right at all temperatures from 0° to 40°C. Since all the previous work is done by passing a "vigorous flow of NO" through the solution, it appears that the nitric oxide pressure did equal one atmosphere.[28] Since Gans supposed that the variation in yield with temperature was due to the extensive shift in the equilibrium position of this reaction with temperature, we can disregard that portion of his proposal. We might be able to justify other portions of the first proposed mechanism if we admit that we don't understand the unusual behavior of the nitric oxide pressure over the solution. However, if we believe our proposal that the monomeric black isomer dimerizes as the concentration of the monomer increases, we can offer a rather different mechanism for the reactions observed. Suppose that the monomer and dimer of the black ion are in equilibrium (using the shorthand notation for which Co is actually $(NH_3)_5Co$)



$$2Co(II) + 2NO \rightleftharpoons \underset{\text{(black monomer)}}{2CoNO^{2+}} \rightleftharpoons \underset{\text{(black dimer)}}{\begin{array}{c} Co-N-O \\ \quad | \\ Co-N-O \end{array}^{4+}}$$

The hyponitrito bridged final product comes from a linkage isomerism reaction of the black dimer:



$$\begin{array}{c} Co-N=O \\ \quad | \\ Co-N=O \end{array} \xrightarrow{\text{slow}} Co-\overset{\overset{O}{|}}{N}=N-O-Co \quad ^{4+}$$

And the hydrolysis reaction occurs from the monomer:

$$Co(NO)^{2+} + 2NO + OH^- \xrightarrow{slow} N_2O + NO_2^- + (CoOH)^{2+}.$$

There are variations on this scheme that also cannot be ruled out, such as direct hydrolysis of the black dimer or reaction of the additional NO with either $(CoN_2O_2)^+$ or uncomplexed $N_2O_2^{2-}$ in the solution. We can make some arguments favoring some aspects of these various schemes, but without additional data we cannot choose among the alternatives.

The various experimental observations about yield as a function of time and concentration can be accommodated by adjusting the rates of the linkage isomerism and hydrolysis reactions. Since the red isomer product also hydrolyzes we can account for the lower yield of red isomer if acetate anions are present rather than nitrate anions. The relative insolubility of the nitrate salt limits the rate of hydrolysis of the red isomer nitrate.

It is clear that this is a complicated sequence of reactions, perhaps more complicated than expected when we began this investigation. A more thorough study of the rapid reactions that occur during the initial exposure of the cobalt(II) solutions to the nitric oxide is the most obvious next step in understanding this system. A study over a much wider range of cobalt concentrations, particularly much more dilute solutions, might provide more quantitative data on the extent of the monomer-dimer equilibrium. It seems quite clear that this is where a lot of interesting chemistry is taking place.

Some Additional Experiment Details

Reagent grade chemicals were obtained and used for all experiments. Most analytical determinations were based on reagents standardized with primary standard KIO_3, $K_2Cr_2O_7$, or sulfamic acid. The reagent ammonium hydroxide bottles were obtained fresh and kept tightly closed to exclude CO_2. Nitric oxide was initially produced by Blanchard's method using $NaNO_2$ and sulfuric acid.[38] For later experiments we used NO from lecture bottles and larger cylinders. The cylinder-supplied nitric oxide always contained noticeable amounts of NO_2. This was removed by bubbling the gas through NaOH solutions, or by passing the gas over a bed of the adsorbent Ascarite©, which is NaOH on asbestos plus an indicator.

The measurements made at temperatures other than room temperature were made with a circulating fluid temperature bath and a jacketed 300 ml flask. The temperatures quoted are ±1 °C for the actual value and varied not more than ±0.3° in any one experiment.

Any experiment which showed signs of oxygen leaking (observation of the "white smoke" of NH_4NO_2 or NH_4NO_3) was stopped and the results were not used for further interpretation.

The visible-ultraviolet spectrophotometric experiments were done using a Cary Model 17 spectrometer. The infrared spectra were obtained on a Perkin Elmer Model 225 spectrometer. Samples were mounted in KBr discs for most routine work. Each important spectrum was checked as a mineral oil mull and a fluorocarbon mull. Gas phase spectra were obtained using a 10 cm pathlength cell with NaCl windows. The magnetic measurements were made using a Princeton Applied Research magnetometer Model FM-1 and the associated equipment. The voltage output of the pressure transducer was measured with both a Heathkit Model IM-120 digital voltmeter to ±1 millivolt and a Hewlett-Packard Model 7100 BM strip chart recorder.

pH measurements were made using a glass electrode vs. calomel using a Beckman Expandomatic Meter. The meter was standardized at pH 7.0 and 10.0 with standard buffers. Potentiometric titration end points were determined with the same meter using a platinum wire sealed in glass vs. calomel. The polarographic experiments were performed with a Princeton Applied Research Model 174 polaragraphic Analyzer.

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PART III

Kinetic Studies of Nitric Oxide Decomposition Over a Cobalt Oxide Catalyst

(Work performed jointly with Vega Sankur,
Fred Shair, and George Gavalas.)

Introduction

Although the important role of nitrogen oxides in photochemical smog formation was recognized some twenty-five years ago, it is the relatively recent national effort in air pollution abatement that has stimulated research in the catalytic decomposition of NO. Platinum had been found in early work to catalyze NO decomposition, but recent work has concentrated on transition metal oxides as possessing higher activity in addition to their lower cost. Fraser and Daniels[1] investigated a number of transition and other metal oxides at temperatures above 600 °C and found the reaction zero order with respect to NO, which they interpreted in terms of strong NO coverage. Yur'eva et al.[2] studied the reaction on several transition metal oxides including Co_3O_4 and Fe_2O_3 in a temperature range 200-800 °C. The reaction rate was found to be second order in NO except with the Co_3O_4 catalyst where the order was in the range 1.5-1.8. The high apparent reaction orders can be explained in terms of inhibition by O_2 which at the time was not recognized. The reaction was carried out in a batch system with recirculation and the level of O_2 in the reacting mixture was not measured but was obviously quite low because of the reaction $2NO + O_2 \rightarrow 2NO_2$ taking place in the colder sections of the apparatus. Shelef et al.[3] studied the decomposition of NO on several transition metal oxides including supported and unsupported Co_3O_4. The reaction rate was fitted with by a power model $r = k_o C_{NO}^{o} \exp(-E/RT)$ and the exponent n was found to be close to one for all but one of the catalysts tested. The inhibiting effect of O_2 was again not taken into account, hence the observed reaction order cannot be interpreted in an absolute sense. An important result of these authors is that unsupported Co_3O_4 is more active than the other catalysts tried by at least a factor of 10^3. Even so, the authors concluded that the catalytic decomposition is too slow for practical applications to automobile exhaust purification.

An important advance in understanding the kinetics of NO decomposition was made by Winter[4] who studied the reaction on as many as forty transition and rare earth oxides. Based on these measurements and his previous work on N_2O decomposition and oxygen exchange, he proposed a mechanism in which the slow steps are the adsorption of NO and the desorption of O_2, resulting in a rate expression $k_o C_{NO}/C_{O_2}$ for NO decomposition. The dependence on O_2 could not be tested because of the reaction $2NO + O_2 \rightarrow 2NO_2$ taking place at the colder section of the batch reactor system. The resulting oxygen concentration in the gas phase over the catalyst surface was not determined.

Boudart et al.[5] have recently reported their work on NO decomposition on several transition metal oxides. Their results indicate first order dependence on NO pressure and strong inhibition by oxygen, i. e. confirm at least qualitatively some of the results of Winter.

The purpose of the present experimental study is to study the rate of NO decomposition as a function of both NO and O_2. The reactor system was designed such that both concentrations could be controlled and determined independently. The catalyst selected was the unsupported Co_3O_4 which was found in the previous work as the most active among the transition metal oxides.

Experimental

The catalyst was prepared by passing dry air through $CoCO_3$ heated in a quartz tube to about 600°C for three hours. The black powder thus obtained was pelletized with a hydraulic press and then crushed. Particles of catalyst used in these studies ranged in size from 48-65 mesh.

The total surface area of the catalyst was measured by means of a modified B.E.T. method.[6] The catalyst used in these studies had a surface area of 32.6 $meter^2$/gram. The reproducibility associated with the preparation procedure is somewhat indicated from the fact that an independently prepared batch of catalyst had a surface area of 36.8 $meter^2$/gram. Atomic absorption measurements indicated that the catalyst contained about 0.021% nickel and less than 0.05% chromium.

The microflow reactor, consisting of a 15 inch length of 1/8 inch diameter stainless steel tube, was placed within a 60 pound cylindrical block of brass. The brass was heated by means of eight 200 watt G.E. Calrod heaters located around the U-shaped microflow reactor. The brass block was surrounded by a two-inch layer of diatomateous earth for insulation. About 0.49 grams of catalyst were placed in the horizontal bottom section of the reactor. Glass wool was inserted to prevent possible movement of the catalyst. The temperature of the brass block was kept constant by means of a proportional controller. After reaching a steady state, the temperatures varied less than ± 0.1C° throughout the reactor and less than ± 0.25C° in time. In order to treat the system as a differential reactor, conversions were kept to less than about 20%. The arithmetic mean of inlet and outlet concentrations were taken to represent the average concentration throughout the reactor for both reactants and products. It can be shown from the determined rate expression that the arithmetic mean differs from the true average concentration by less than 3% at the highest conversions reported (20%). In these studies the average residence time associated with flow through the reaction zone ranged from 0.1 to 1 second.

The composition of the effluent stream was determined by means of a Loenco model 15-B gas chromatograph equipped with thermal conductivity detectors. The chromatograph column consisted of a 10 feet 1/8 inch stainless steel tube packed with molecular sieve type 5 A. Complete separation was obtained between N_2, O_2, and NO, but NO_2 could not pass through the column. Experiments were conducted with NO supplied from a cylinder of commercially prepared 5% NO in helium mixture; the major impurity was NO_2 present at concentrations somewhat less than 400 ppm. The NO_2 in the inlet stream was neglected since it represented less than 1% by volume of the NO initially present and its decomposition was calculated to be negligible under reactor conditions. The second major impurity was N_2 present at 300 ppm and was taken into account during data reduction; this correction amounted to no more than 10% in the worst case.

Carbon dioxide was present at about 100 ppm, and the concentrations of CO and N_2O were less than 25 ppm.

The pressure within the reactor was kept constant at atmospheric and the pressure drop through the reactor was negligible. Although concentrations of NO, O_2, and N_2 were measured, the rate determinations were based upon the appearance of N_2 in order to avoid correcting for the loss of O_2 and NO by the reaction $2NO + O_2 \rightarrow 2NO_2$ occurring downstream of the reactor. Only about 10 minutes were needed for reaching a steady state after the concentration of NO was changed in the inlet stream. Three separate readings of concentrations in the outlet stream were determined at each point. Concentration readings were accepted when the maximum disagreement between any of the three readings were less than 2%. Preliminary experiments had been conducted with an inlet concentration of NO equal to 0.5% and at temperatures high enough for the reaction to reach completion; the amounts of O_2 and N_2 in the effluent stream were equal indicating negligible formation of N_2O.

Results and Discussion

The decomposition of NO on Co_3O_4 was investigated in the temperature range 350 °C to 500 °C, however, the catalyst was found to be active at temperatures as low as 300 °C. The catalyst showed no signs of deactivation in the span of six months during which about 250 hours of testing were conducted.

As indicated in Figure 1, the rate of NO decomposition is well described by

$$\frac{1}{r} = a + b \frac{C_{O_2}}{C_{NO}} \tag{1}$$

or equivalently

$$r = \frac{k C_{NO}}{K_1 C_{NO} + K_2 C_{O_2}} \tag{2}$$

The values of $a = K_1/k$ and $b = K_2/k$ at four different temperatures were evaluated by plotting $1/r$ vs. C_{O_2}/C_{NO}, as shown in Figure 2. The value of K_1C_{NO} was found to be small compared to that of $K_2C_{O_2}$ in the range $C_{O_2}/C_{NO} > 0.02$, thus except for very low conversions the rate can be approximately described by

$$r = k_o \frac{C_{NO}}{C_{O_2}} \tag{3}$$

where $k_o = k/K_2$.

An Arrhenius plot of this constant, k_o, shown in Figure 3, yields an activation energy of 26.8 ± 0.5 kcal/g-mole. This activation energy is similar to the values obtained by Yur'eva, et al. and Shelef, et al.[2,3] Boudart found a value of 22.5 kcal/g-mole^{-1} at the higher temperatures.[5] This is expected if the general mechanism discussed below is a correct description of the reason for the difference in order observed.

Figure 1. Reciprocal rate vs. oxygen-nitric oxide ratio at one temperature.

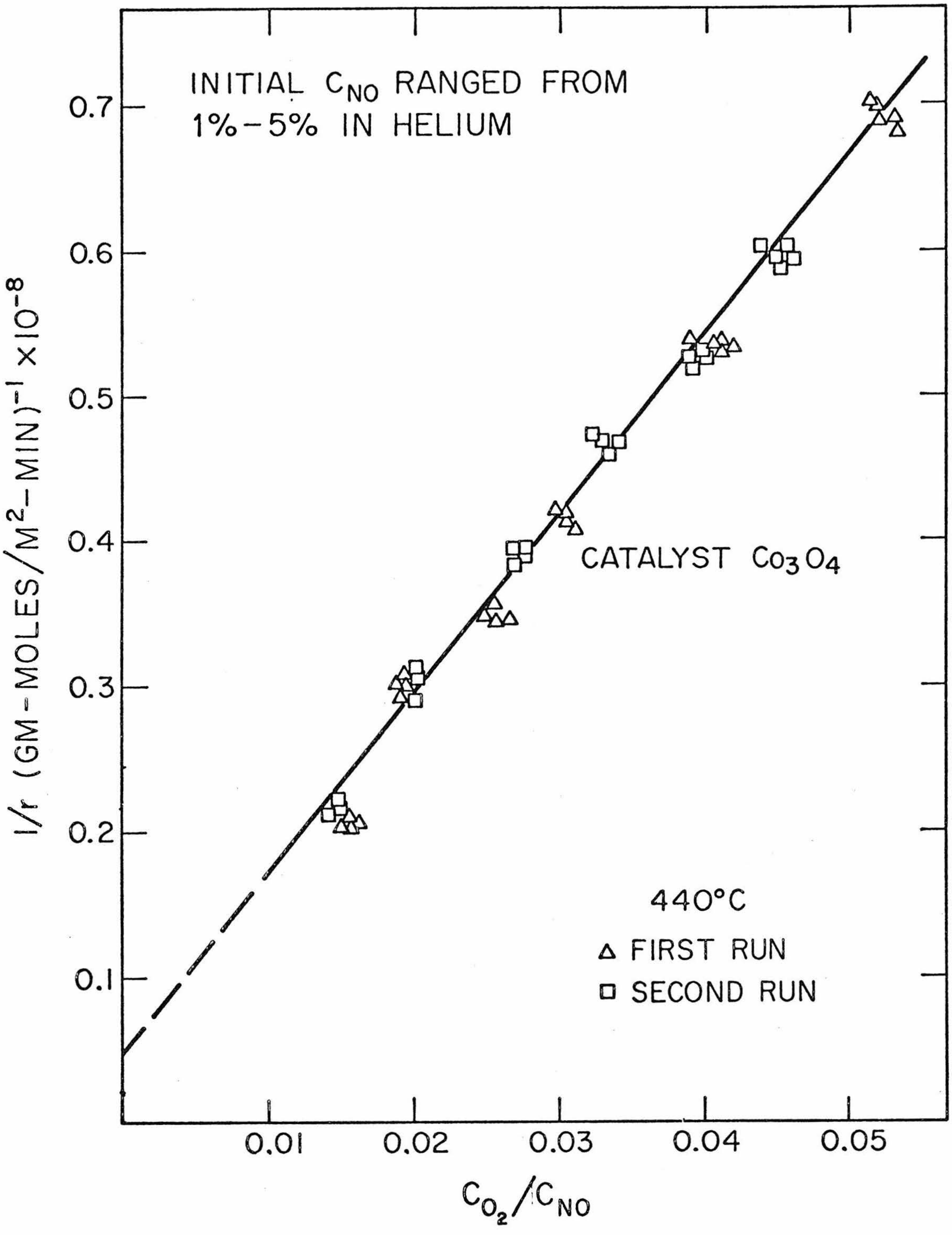

INITIAL C_{NO} RANGED FROM
1%-5% IN HELIUM
CATALYST Co_3O_4
440°C
△ FIRST RUN
□ SECOND RUN
$1/r$ (GM-MOLES/M^2-MIN)$^{-1}$ ×10^{-8}
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.01
0.02
0.03
0.04
0.05
C_{O_2}/C_{NO}

Figure 2. Reciprocal rate vs. oxygen-nitric oxide ratio at several temperatures.

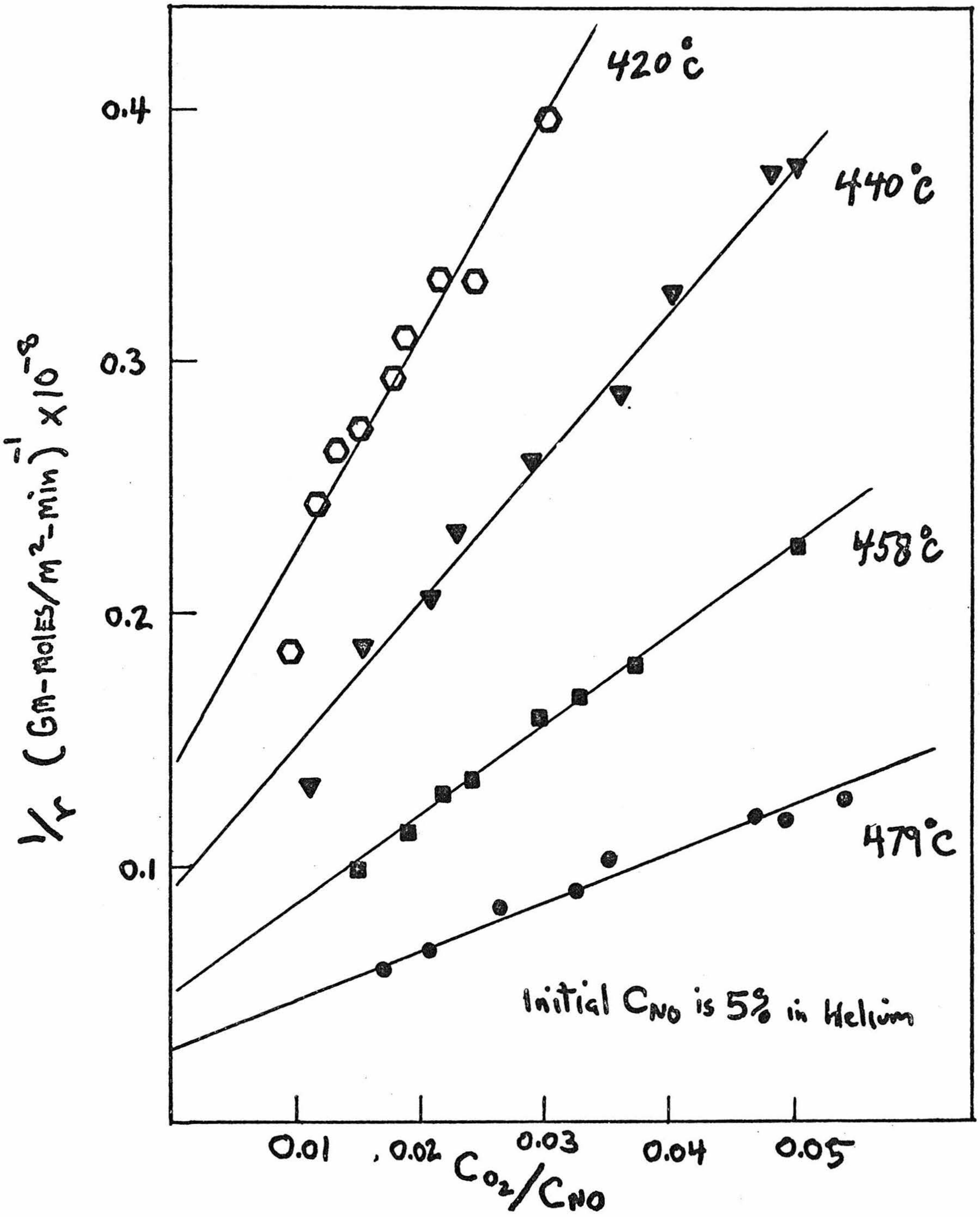
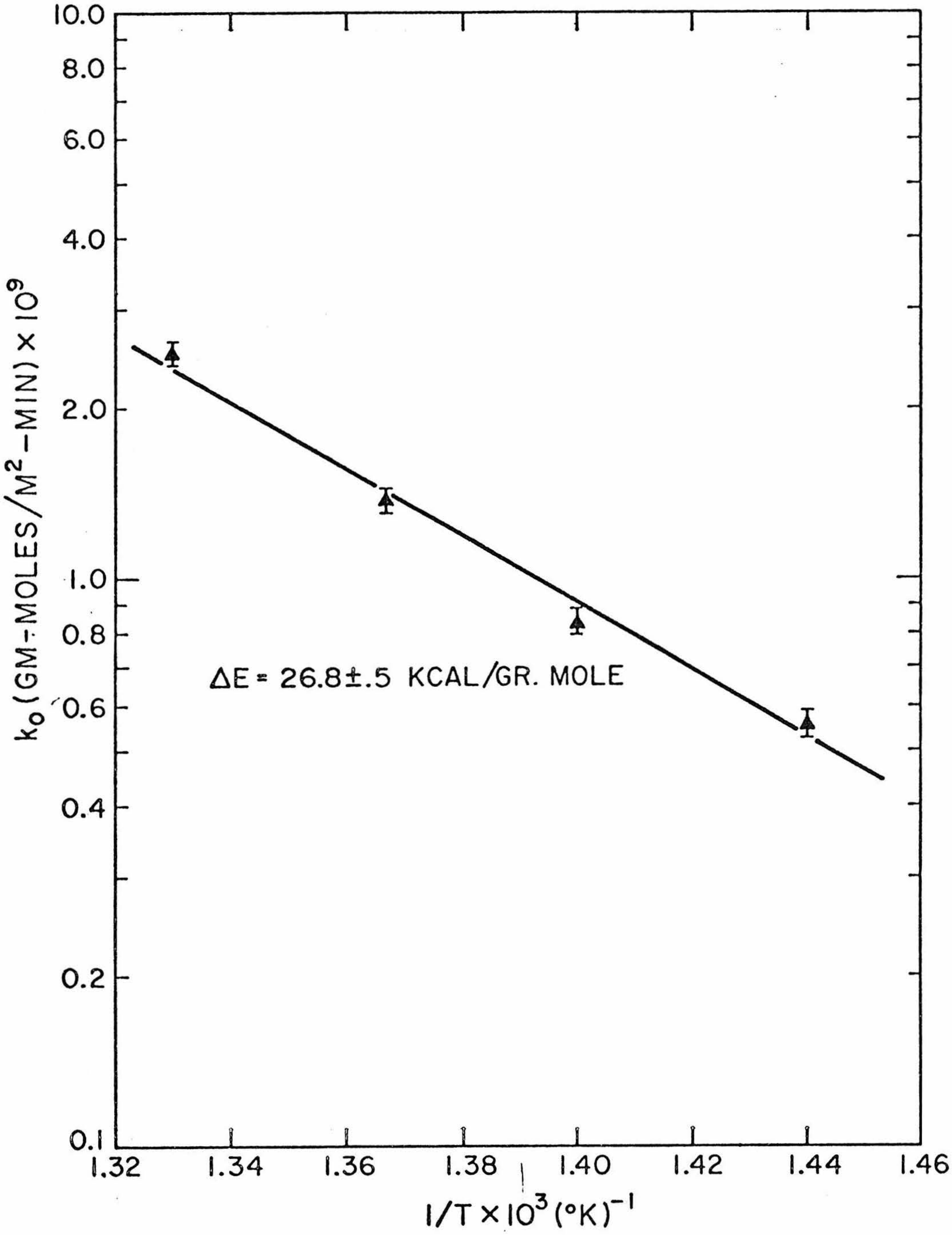

420°C
440°C
458°C
479°C
0.4
0.3
0.2
0.1
$1/r$ (GM-MOLES/M^2-MIN$)^{-1}$ x 10^{-8}
0.01
0.02
0.03
0.04
0.05
C_{O_2}/C_{NO}
Initial C_{NO} is 5% in Helium

Figure 3. Arrhenius plot for inhibited reaction rate constant.


10.0
8.0
6.0
4.0
2.0
1.0
0.8
0.6
0.4
0.2
0.1
k_o (GM-MOLES/M^2-MIN) × 10^9
ΔE = 26.8±.5 KCAL/GR. MOLE
1.32
1.34
1.36
1.38
1.40
1.42
1.44
1.46
1/T × 10^3 (°K)$^{-1}$

For the temperature range we studied, we find the reaction to be approximately zero order with respect to NO in the limit of zero conversion. This is shown in Figure 1. Each set of points at a particular ratio of O_2 to NO is for initial concentrations of NO from 1 to 5%. Each set of points for a given initial concentration extrapolates to approximately the same point at $C_{O_2}/C_{NO} = 0$, so we observe no dependence of the initial rate on NO concentration. This is in contrast to the work of Boudart.[5] However, we note that Boudart worked at much higher temperatures, 600 and 700°C, and that the pretreatment and analytical methods are subject to some uncertainty.

While the data we have can be fitted to a rate law as described by Winter,[4] this law could not account for the results of Boudart. On the other hand, the rate law used by Boudart,

$$r = \frac{Nk(NO)}{1 + \alpha K(O_2)} \qquad (8)$$

where N = Avagadro's Number

k = reaction rate constant

$(NO), (O_2)$ = molar concentration, mol cm^{-3}

K = adsorbtion equilibrium constant in $atm.^{-1}$

α = conversion in atm. mol^{-1} cm^3.

cannot explain our data, either with the values obtained by them for k and K or in the general case. At zero conversion, this expression shows the rate should vary as the NO concentration.

There is a very general form of rate law for decomposition of gases on surfaces. This law is derived from considerations of the form of adsorption isotherms and not from considerations of elementary reactions. We think both our results and Boudart's can be considered as special cases of the form;

$$r = \frac{k[NO]}{1 + a[NO] + b[O_2]} \tag{9}$$

where k is a rate constant and a and b are adsorption equilibrium constants.

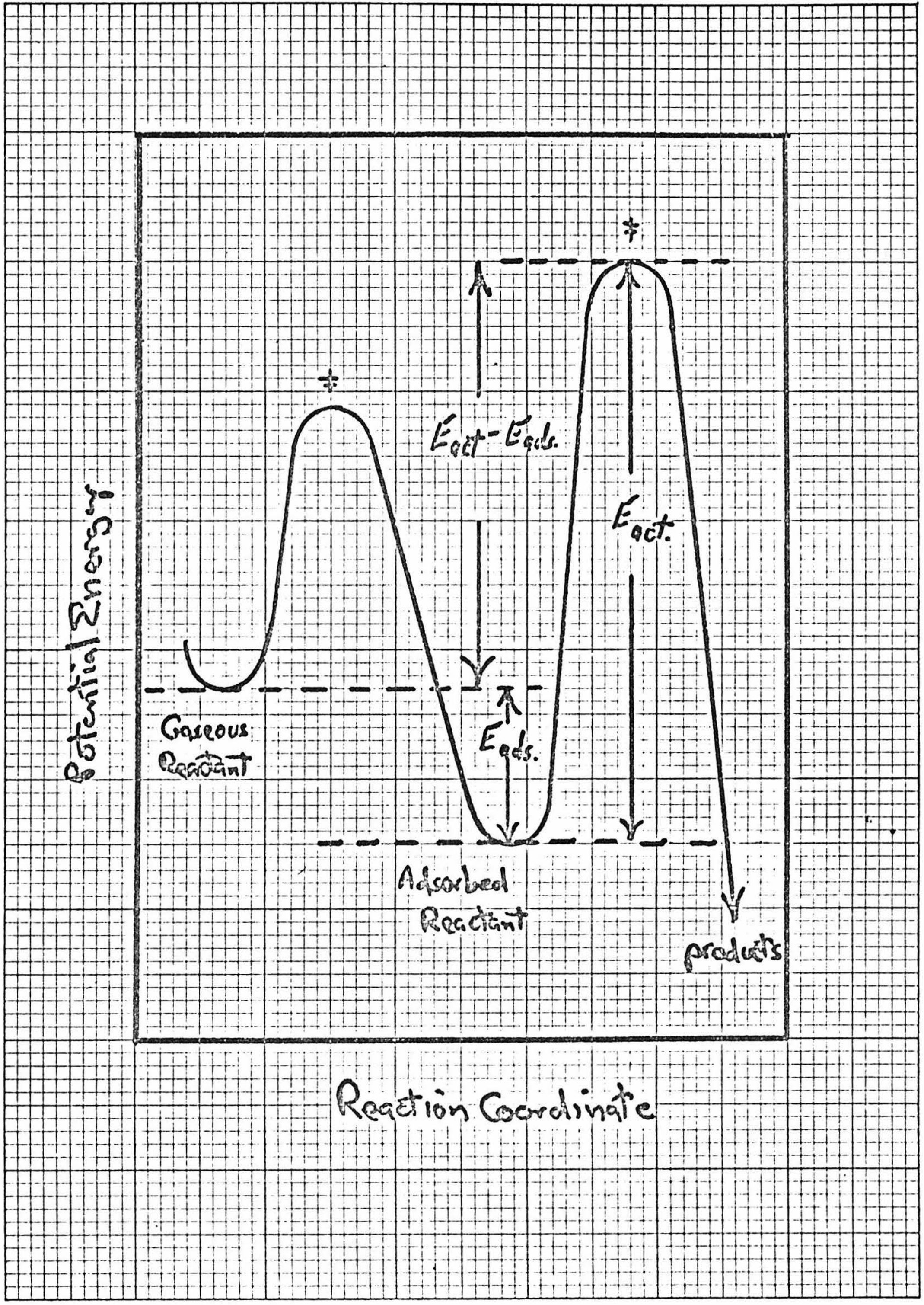
This form of the rate law is observed for the decomposition of, for example, N_2O on Pt and Ag wires. At 440 °C the adsorption equilibria are both quite favorable and the last two terms in the denominator are large compared to 1, and we obtain the rate law (1). At 600 °C the adsorption equilibria are much less favored and the adsorption of NO is much less than of O_2 so that the important terms in the denominator are $1 + b[O_2]$. This reduces the general form (9) to that of Boudart (8). These changes in the rate expression are commonly called the "high pressure" limit and the "low pressure" limit of the general rate law for a unimolecular reaction inhibited by adsorption of product. It is possible that if we made measurements at much lower NO pressures or Boudart's group worked at higher pressures, the observed rate laws would change toward the more general form. However, it is more likely that this change in rate law would be more easily observed in the temperature region between 500° and 600 °C at the pressures we have used.

In addition to the difference in rate laws observed, the difference in activation energies is also understandable as the result of the different conditions of applying the general form (9).

In the "high pressure" limit, the activation energy is that due to the chemical reaction and is called the "true" activation energy. In the "low pressure" limit, the observed rate constant is the product of both the rate constant of the chemical reaction and the equilibrium constant of the adsorption equilibrium and the activation energy is the activation energy of the chemical reaction reduced by the heat of adsorption of the reaction. This relationship can be illustrated with a potential energy diagram, as shown in Figure 4. A reaction of a molecule first carries it over the initial barrier to the adsorbed state at an energy, E_{ad}, lower than the initial state. Then the chemical reaction requires the molecule to go over the next barrier, E_{act}. If the pressure is low, most molecules are in the unadsorbed state and need energy $E_{act} - E_{ad}$ to react. At high pressures, the reacting molecules start in the adsorbed state, and need energy E_{act} to pass over the barrier.

Similarly, the strongly adsorbed inhibitor can also modify the activation energy. Simply stated, this occurs because a molecule of inhibitor must be desorbed so that a molecule of reactant can become adsorbed to react. Since we do not really have enough experimental data to sort out these various factors, we cannot attribute the difference in the observed activation energy to any one item. However,

Figure 4. Potential energy diagram for reaction of adsorbed molecule.


‡
‡
Eact - Eads.
Eact.
Eads.
Gaseous Reactant
Adsorbed Reactant
products
Potential Energy
Reaction Coordinate

the fact that the activation energy observed by Boudart is significantly lower than we observed, it is consistent with the suggested general expression (9).

Above 900 °C the reaction,

$$2Co_3O_4 \rightleftharpoons 6CoO + O_2$$

is very rapid in air.[8] Since the p_{O_2} is 0.2 atm, this reaction is likely to proceed rapidly at lower temperature in the absence of O_2. (If we knew the ΔH of this reaction as a function of temperature in this temperature range, we could calculate the equilibrium pressure of O_2 as a function of temperature.) This reaction should limit studies of the decomposition of NO over Co_3O_4 to temperatures below the value where the equilibrium is rapidly attained. It is this reaction which troubles Boudart at or above 700 °C, apparently.

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