six-coordinate bis adduct are unconvincing, and in fact experimental evidence of the formation of a bis adduct in this system has been reported.[16]

Finally we have examined the behavior of Ni(saloph) and Co(saloph) in the presence of pyrrole. Pyrrole, like imidazole and pyrazole, is an aromatic molecule but it is a much weaker base since it lacks a nitrogen lone pair which is not a part of a conjugated π-system. In fact, it is interesting to note that protonation of pyrrole preferentially occurs at a carbon atom rather than at the nitrogen.[17] The electronic spectra of Co(saloph) and Ni(saloph) are unaffected by up to a 1000-fold excess of pyrrole. We conclude then that the pyrrole nitrogen as well as N-1 of imidazole and N-1 of pyrazole are incapable of significant coordination to the acids **4** and **5**.

Acknowledgment. This research was supported by Grant GM 18357 from the National Institutes of Health.

References and Notes

(1) B. S. Tovrog and R. S. Drago, *J. Amer. Chem. Soc.*, **96**, 2743 (1974).

(2) H. Zimmerman and H. Geisen Felder, *Z. Elektrochem.*, **65**, 369 (1961).

(3) A. F. Bedford, P. B. Edmondson, and C. T. Mortimer, *J. Chem. Soc.*, 2927 (1962).

(4) J. D. Cox, *Tetrahedron*, **19**, 1175 (1963).

(5) For an independent and more detailed discussion of imidazole coordination, which is in agreement with our position, see R. J. Sundberg and R. B. Martin, *Chem. Rev.*, **74**, 471 (1974).

(6) B. B. Wayland and W. L. Rice, *J. Chem. Phys.*, **45**, 3151 (1966).

(7) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 2879 (1967).

(8) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2522 (1968).

(9) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, **93**, 1374 (1971).

(10) B. O. West, *J. Chem. Soc.*, 395 (1954).

(11) N. Joop and H. Zimmermann, *Z. Elektrochem.*, **66**, 541 (1962).

(12) A. Perotti and M. Cola in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N.Y., 1965, p 249.

(13) Sufficient Co(saloph) to give a 1×10^{-3} *M* solution would not dissolve in a 0.5 *M* solution of pyrazole in dichloromethane. However, upon exposure of this mixture to air, the cobalt complex readily dissolved.

(14) Considering Figure 3 of ref 1 and assuming a pmr probe temperature of 35° we calculate that a 1 *M* imidazole solution was utilized to obtain the data point at 0% Ni(saloph). At this imidazole concentration Ni(saloph) is insufficiently soluble to produce $[\text{Ni(saloph)}]/[\text{imidazole}] > 0.02$. Consequently in order to span the range of complex concentrations reported some dilution was required. Further speculation about the details of the procedure that led to dilution is unwarranted.

(15) Another indication that insufficient precautions were taken by the authors of ref 1 in handling Co(saloph) solutions occurs in their claim that Co(saloph) produces changes in the pmr spectrum of pyrazole similar to the changes produced by Ni(saloph). However, we have observed that Co(saloph) will not dissolve sufficiently in a dichloromethane–pyrazole solution (in the absence of oxygen) to allow such data to be obtained.[13] Exposure of such mixtures to air causes the dissolution of the cobalt complex but this produces no alterations of the pmr spectrum of the base.

(16) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 5752 (1970).

(17) R. A. Jones, *Advan. Heterocycl. Chem.*, **11**, 383 (1970).

Structure and Reactivity of Cobalt–Nitrosyl Complexes in Y-Type Zeolites

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Abstract: Nitric oxide was allowed to react with Co^{2+} ions, as well as with cobalt ammine complexes, in cobalt-exchanged zeolites. The formation of $[Co^{II}(NO)_2]^{2+}$, $[Co^{II}(NH_3)(NO)_2]^{2+}$, and $[Co^{III}(NH_3)_nNO]^{2+}$ was suggested from the infrared and adsorption data. In the latter complex n is probably equal to 5. Infrared absorption bands for N–O stretching vibrations were observed at 1830 and 1910 cm^{-1} for $[Co^{II}(NO)_2]^{2+}$, at 1800 and 1880 cm^{-1} for $[Co^{II}(NH_3)(NO)_2]^{2+}$, and at 1710 cm^{-1} for the $[Co^{III}(NH_3)_nNO]^{2+}$ complex. A bond angle of 123° was estimated for the ON–Co–NO moiety in the dinitrosyl complexes from ir band intensities. When $[Co(NO)_2]^{2+}$ was thermally decomposed at 200°, N_2, N_2O, and NO were observed as products. The intramolecular reaction of $[Co^{III}(NH_3)_nNO]^{2+}$, as well as its intermolecular reaction with gas phase NO, was followed at 23°, and the two reactions were found to yield N_2, N_2O, and $[Co^{III}(NH_3)_nNO_2]^{2+}$. Isotope labeling proved that N_2 was produced by the reaction of the NO^- ligand with NH_3, whereas N_2O and NO_2 were produced by the disproportionation reaction of the NO^- ligand with two nitric oxide molecules. It was observed that the disproportionation reaction was favored by a greater pressure of NO over the zeolite. The production of NO_2 and its coordination with cobalt prevented further formation of the nitrosyl complex and hence destroyed the catalytic activity.

The importance of transition metal complexes in the dissociation and reduction of nitric oxide has led to a number of investigations of nitrosyl complexes in heterogeneous systems.[1-6] Nitric oxide has also been used as a probe to study the state of supported transition metal ions. It has been shown that Cu^+, Ag^+, Ni^{2+}, Fe^{2+}, and Cr^{2+} ions form complexes with NO in zeolites.[1-5] In each of these cases the data may be interpreted in terms of either covalent bonding or the donation of an electron from the nitric oxide to the metal ion. The latter tends to strengthen the N–O bond and to increase the stability of the nitric oxide molecule.

Several nitrosyl complexes of rhodium and cobalt are known to have a high electron density on the NO ligand.[7] Such complexes are characterized by an M–N–O bond angle of about 120° and an N–O stretching frequency in the range 1550–1700 cm^{-1}. By way of contrast the cationic nitrosyl ligands of these same metal ions are nearly linear with an N–O stretching frequency near 1850 cm^{-1}. The decrease in the N–O bond strength for the anionic nitrosyl is associated with the additional electron in a π^* antibonding orbital.

Recent studies on the bent Co–NO moiety have demonstrated that the nitrosyl ligand is subject to reaction with either molecular oxygen or free nitric oxide.[8,9] Alternately, the nitrosyl ligand may react with another ligand such as ammonia, forming N_2 and H_2O. One would, of course, hope to observe the direct dissociation of the nitric oxide; however, this has yet to be accomplished at moderate temperatures. The reactions of interest may be summarized as

$$L_nM\text{–}NO + 2NO \longrightarrow L_nM\text{–}NO_2 + N_2O \tag{1}$$

$$L_nM\text{–}NO \longrightarrow L_{n-1}M + N_2 + H_2O \tag{2}$$

$$L_nM\text{–}NO + NO \longrightarrow L_nM + N_2 + O_2 \tag{3}$$

where in this study $M = Co^{2+}$ and $L = NH_3$.

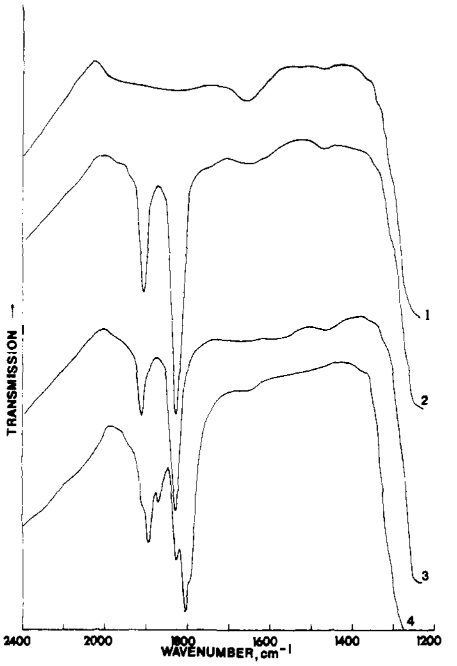


Figure 1. Infrared spectra of a CoY zeolite: (1) after degassing at 500°; (2) 1 hr after introducing 50 Torr of NO into the cell; (3) after evacuating the cell for 1 hr at 150°; (4) after introducing a 50:50 mixture of ^{14}NO:^{15}NO to a degassed sample.

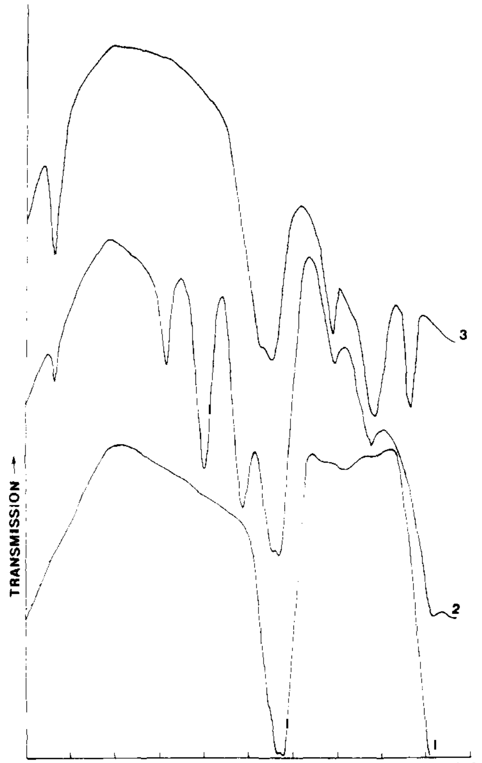


Figure 2. Infrared spectra of a CoY zeolite: (1) after degassing at 500°, addition of 200 Torr of NH_3 and the removal of excess NH_3 by evacuation; (2) 15 min after the introduction of 50 Torr of NO; (3) 5 hr after the NO addition.

It has been shown that cobalt ions in a Y-type zeolite may form fully coordinated complexes with ligands such as methyl isocyanide.[10] Vansant[11] has recently demonstrated that in the presence of excess ammonia the relationship between the NH_3 uptake and the Co^{2+} content of a Y-type zeolite was linear with a slope corresponding to 5.6 NH_3 molecules/Co^{2+}. There is also epr evidence for the formation of complexes such as $[Co^{III}(NH_3)_5O_2]^{2+}$ and $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ within the zeolite framework.[12,13] In the present work NO has been complexed with Co^{2+} which is bound either to the lattice oxide ions or to one or more ammonia molecules. The vast difference in the reactivity of the nitrosyl ligand in these two types of complexes emphasizes the potential of supported transition metal complexes in heterogeneous catalysis. On the other hand, the problem of poisoning by a nitro ligand, which is a reaction product, has become very evident as a result of this study.

Experimental Section

The NaY samples were exchanged by using two different procedures. Two samples were prepared by exchanging 2 g of NaY zeolite supplied by the Linde Co. (lot no. 13544-76) in 250 ml of 0.007 and 0.041 *M* $Co(NO_3)_2$. These are designated CoY (1) and CoY (2), respectively. For CoY (3), the pH of the solution was maintained at 4.0 throughout the exchange procedure to prevent the possible formation of a cobalt hydroxide precipitate within the zeolite. This was necessary due to the high concentration of the $Co(NO_3)_2$ solution (0.14 *M*). These procedures produced samples which had 10, 50, and 77% of the sodium ions exchanged for Co^{2+} ions. This corresponded to 2.8, 14.0, and 21.7 Co^{2+} ions per unit cell for CoY (1), CoY (2), and CoY (3), respectively. An exchange temperature of 80° was maintained for all three samples. The CoY samples were degassed at room temperature briefly, and then in 100° increments to 500° under vacuum (5×10^{-5} Torr).

The ^{14}NO gas was obtained from the Matheson Corporation and contained small amounts of N_2O and NO_2 as impurities. These were removed by repeated distillation followed by the collection of the NO at −196°. The ^{15}NO was 99% enriched in ^{15}N.

The infrared cell used to carry out this work has been described previously.[3] The infrared spectra were recorded with a Beckman IR-12 spectrophotometer, which was usually operated in the transmittance mode. The slit width was chosen such that a maximum resolution of 3 cm^{-1} was maintained. The zeolite plates were formed under a pressure of 15 tons/in.^{2} with a resulting density of 10 mg/cm^2. The maximum single beam transmission for each sample was approximately 40%. All spectra were recorded at room temperature.

A static reactor consisting of a 500-ml Pyrex bulb connected by a 4-mm stopcock to the vacuum system was used to carry out the mass spectrometry measurements. The CoY sample was placed at the bottom of a 25-mm o.d. well which extended 3 in. below the bulb. Samples ranging from 0.3 to 0.5 g were placed at the bottom of the reactor where they were given the standard pretreatment. The products of the reaction were analyzed with a CEC-214 residual gas analyzer. The sensitivity of the instrument was determined for each of the gases that was analyzed.

A gravimetric adsorption experiment was carried out in a 25-mm Pyrex tube which was approximately 80 cm in length. A sample of CoY of a known weight was suspended inside the tube from a quartz spring with a force constant of 1.31 mg/mm. By measuring the extension of the spring upon the addition of nitric oxide or ammonia, it was possible to determine the average number of molecules coordinated to each cobalt ion in the zeolite.

Results

Infrared Studies. Figure 1 shows the ir spectra obtained for a CoY (2) sample during various stages of NO adsorption. Curve 1 was obtained after the standard pretreatment. Except for several relatively small windows, the Y-type zeolite is opaque to infrared radiation below 1200 cm^{-1}. Curve 2 shows the spectrum of the CoY (2) after 50 Torr of NO was added. The strong band at 1830 cm^{-1} and the medium intensity band at 1910 cm^{-1} were not affected by degassing the CoY zeolite at room temperature. Curve 3 shows the spectrum obtained after the sample was degassed under vacuum at 150° for 1 hr. Earlier work[14] has shown that adsorption of nitric oxide on NaY zeolites at 23° yields no infrared bands other than that of physically adsorbed NO.

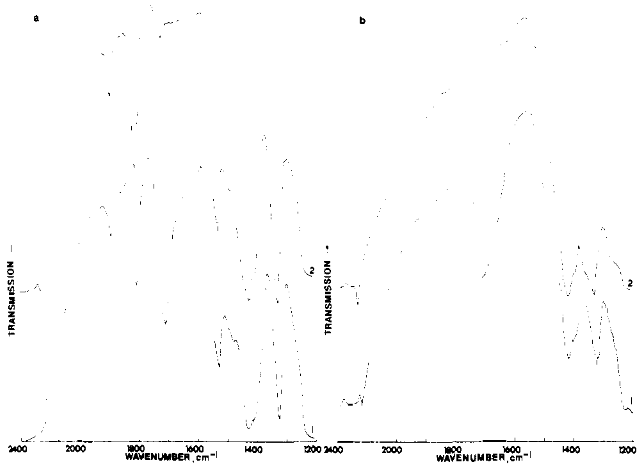


Figure 3. (a) Infrared spectra of a CoY zeolite after complexing with ND_3 followed by the removal of excess ND_3 *via* evacuation: (1) 15 min after the addition of 50 Torr of NO; (2) 2 hr after the addition of NO. (b) Infrared spectra of a CoY zeolite after complexing with ND_3, followed by the removal of excess ND_3 *via* expansion: (1) 15 min after the addition of 50 Torr of NO; (2) 5 hr after the addition of NO.

The addition of less than 10 Torr of NO produced a spectrum in which the bands at 1830 and 1910 cm^{-1} were proportionally weaker. Studies carried out using CoY (1) and CoY (3) yielded the same spectrum with the intensity of the two bands being approximately proportional to the exchange level of the different samples.

Curve 4 was recorded after a second CoY (2) sample was given the standard pretreatment and 50 Torr of a 50% ^{14}NO-50% ^{15}NO mixture was introduced. Infrared bands at 1810, 1830, 1880, and 1900 cm^{-1}, as well as two shoulders at 1800 and 1910 cm^{-1} appeared in the N-O stretching region.

Figure 2 shows the ir spectra taken at various stages in the preparation of the nitrosyl complex from cobalt ammines. Curve 1 was obtained after the addition of 200 Torr of NH_3 to a CoY (3) sample. The band at 1640 cm^{-1} corresponds to the antisymmetric deformation vibration of complexed NH_3. After allowing the ammine complex to form for several hours, the excess NH_3 was removed by evacuating for 30 sec. Curve 2 was observed 15 min after the addition of 50 Torr of NO. New bands appeared at 1430, 1520, 1710, 1800, 1880, and 2240 cm^{-1}. Curve 3 was recorded 5 hr after the nitric oxide addition. The bands at 1430, 1520, and 2240 cm^{-1}, as well as a new band at 1330 cm^{-1}, gradually increased in intensity after the initial introduction of nitric oxide until they reached a maximum after 5 hr, and thereafter their intensities remained constant. The band at 1640 cm^{-1} remained essentially constant while the bands at 1710, 1800, and 1880 cm^{-1} gradually decreased and disappeared after 5 hr.

In an attempt to observe more clearly the band at 1710 cm^{-1} ND_3 was used to form the complex which will be designated as the $[Co^{III}(ND_3)_nNO]^{2+}$ complex. The ND_3 antisymmetric deformation vibration appears at 1210 cm^{-1} which is well separated from all of the significant bands. Figure 3a shows the spectrum obtained after the pretreatment of a CoY (2) sample and complexation with ND_3. Removal of the excess ND_3 was again accomplished by evacuation for 30 sec. Curve 1 was recorded 15 min after the addition of 50 Torr of NO. Curve 2 was obtained 2 hr after the addition of nitric oxide. It is apparent that the band at 1710 cm^{-1} decreased with time while the bands at 1330, 1430, and 1520 cm^{-1} which correspond to a nitro complex[15] increased. The band at 2240 cm^{-1} also showed an increase in intensity.

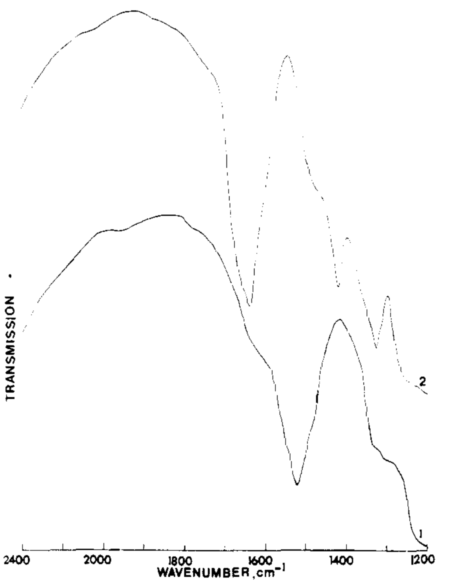


Figure 4. Infrared spectra of a CoY zeolite: (1) after the addition of NO_2; (2) after the addition of 200 Torr of NH_3, removal of the excess NH_3 by expansion, and addition of 50 Torr of NO_2.

In a separate experiment, ^{15}NO was substituted for ^{14}NO in the preceding reaction. The infrared spectrum obtained was essentially the same as that shown in Figure 3a, curve 2, except that all the peaks were shifted to lower wave numbers (1300, 1400, 1490, 1680, 1770, 1850, and 2180 cm^{-1}). This shift is in good agreement with a calculated isotope shift for an N-O bond of 28.9 wave numbers. The shift of 60 wave numbers for the band originally at 2240 cm^{-1}, which corresponds to $^{15}N_2O$, can be explained by noting that two ^{15}N's are incorporated in this molecule. The band at 2240 cm^{-1} is assigned to a N-N stretching vibration. If both are substituted with ^{15}N, the shift would be expected to double.

To determine the effect of excess ammonia on the complexes a second experiment was undertaken in which the ND_3 was removed by expanding it into a large volume. By this method, the pressure of the ND_3 was reduced to approximately 3 Torr. This was done to provide a more complete coordination of the cobalt ions with ND_3 ligands, presumably forming a hexaammine cobalt complex. Figure 3b shows the ir spectra obtained after 50 Torr of nitric oxide was added. Curve 1 was recorded 15 min after the NO addition. Curve 2 was recorded 5 hr after the NO addition. The absence of bands between 1800 and 1880 cm^{-1} indicates that the complex responsible for these bands has less than the maximum ammonia coordination. Apparently expansion of the ammonia does not remove a significant amount of complexed ND_3, and all of the complexes are in the $[Co^{III}(ND_3)_nNO]^{2+}$ form. The growth of bands at 1330 and 1430 cm^{-1} accompanied by a decrease in the band at 1710 cm^{-1} indicates that the nitro complex is again being produced by a reaction of the nitrosyl ligand.

To verify that NO_2 may be produced in the reaction of nitric oxide on the cobalt hexaammine complex, NO_2 was added to the cobalt zeolites, and the resulting spectra are shown in Figure 4. Curve 1 was obtained 15 min after the addition of 50 Torr of NO_2 to a CoY (2) sample. The appearance of a band at 1520 cm^{-1} corresponds well with the band observed in curve 2 of Figure 2. Curve 2 of Figure 4 was obtained after the addition of NO_2 to the hexaammine-cobalt(II) complex. The removal of the excess NH_3 was

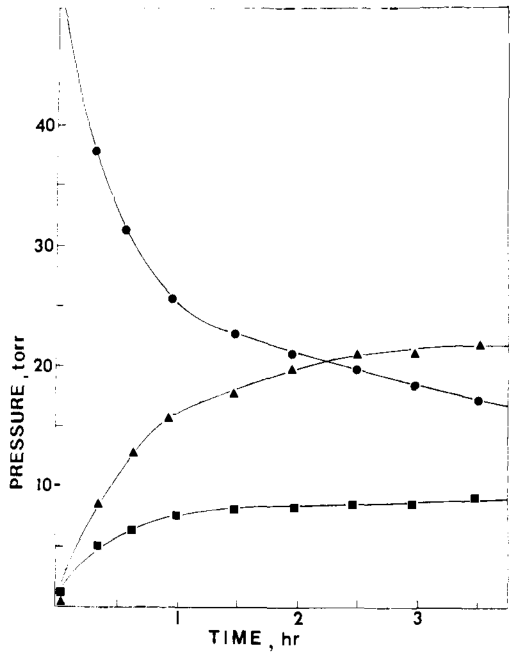


Figure 5. Plot of the partial pressure of N_2 (■), NO (●), and N_2O (▲) *vs.* time for the reaction of NO with a cobalt ammine complex in a CoY zeolite.

achieved by expansion. The addition of 50 Torr of NO_2 resulted in the formation of bands at 1330 and 1430 cm^{-1}.

Mass Spectrometry Studies. CoY (2) and CoY (3) samples were activated as previously described, and nitric oxide was added. An analysis of the gas phase in the reactor was carried out after the cobalt nitrosyl complex in the zeolite had been heated to various temperatures. At 23° only NO was present in the gas phase over the catalyst. After heating the sample to 200° for 1 hr, however, approximately half of the NO had been converted into N_2 and N_2O in equal quantities. No O_2 was detected. The results for the two types of samples were identical.

A CoY (2) sample was activated using the standard pretreatment conditions in the reactor. Approximately 200 Torr of NH_3 was adsorbed to produce the hexaammine complex. Excess NH_3 was expanded off and 50 Torr of NO was added to the system. The composition of the gas phase *vs.* time is plotted in Figure 5. The amount of NO in the gas phase in the reactor decreased while the amount of N_2O and N_2 increased. Addition of another 50 Torr of NO after the reaction had reached completion failed to produce any further reaction.

An additional experiment was carried out on an activated CoY (2) sample in which only 5 Torr of nitric oxide was allowed to react with the hexaammine cobalt complex. After 2 hr of reaction, the gas phase contained only N_2 and NH_3. Alternately, 5 Torr of NO was added to the zeolite first and after sufficient time for coordination had elapsed 50 Torr of NH_3 was added. Again, after 2 hr analysis of the gas phase in the reactor showed only N_2 and NH_3.

In a separate experiment, ^{15}NO was used in place of ^{14}NO to determine whether the molecular nitrogen was formed from the direct dissociation of NO or by the reaction of NO and NH_3. Upon treating the ^{15}NO with the hexaammine cobalt complex, it was found that the N_2 and N_2O produced by the reaction were in the form $^{14}N^{15}N$ and $^{15}N^{15}NO$. A trace amount of $^{15}N^{15}N$ was observed, but this was probably due to the dissociation of N_2O in the mass spectrometer. The same reaction was studied using $^{15}NH_3$ and ^{14}NO. The gas phase products were $^{15}N^{14}N$ and $^{14}N_2O$.

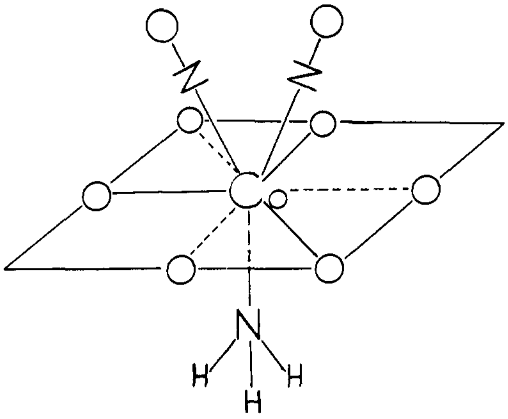


Figure 6. Conception of the $[Co(NH_3)(NO)_2]^{2+}$ complex as it exists in a Y-type zeolite.

Adsorption Experiments. A CoY (2) sample was suspended from a quartz spring in an evacuated Pyrex tube. After activation using the standard pretreatment, 70 Torr of nitric oxide was added and the excess gas was removed by evacuation at 25°. It was found that the cobalt nitrosyl complex in the CoY (2) sample had 1.9 NO molecules per Co^{2+} ion. Evacuation of the sample tube at temperatures up to 70° produced no change in the NO to Co^{2+} ratio.

To determine the stoichiometry of the complex formed by the addition of excess ammonia and evacuation at 25°, a CoY (3) sample was activated and complexed with NH_3. The excess NH_3 was removed by evacuation at 23° for 15 hr. The prolonged evacuation was carried out to destroy the hexaamminecobalt(II) complex. The results showed that there were 1.2 ammonia molecules per Co^{2+} ion. Subsequent addition of 50 Torr of NO followed by brief evacuation indicated that 1.9 NO ligands were added per Co^{2+} ion.

It is perhaps worth noting that in the presence of excess NH_3 at a pressure of 3 Torr, 10.1 molecules of NH_3 were observed per Co^{2+} ion. This is expected since the zeolite itself adsorbs ammonia.

Discussion

From the adsorption experiment, it is apparent that the cobalt nitrosyl complex in a Y-type zeolite exists in the form $[Co(NO)_2]^{2+}$. Since two infrared bands in the N-O stretching vibration region are present, one must correspond to a symmetric vibrational mode and the other to an antisymmetric vibrational mode. From a consideration of dipolar interactions, it is most likely that the in-phase stretching mode has a higher frequency than the out-of-phase stretching mode. In this case, the 1910-cm^{-1} band would correspond to ν(N-O)sym while the band at 1830 cm^{-1} can be assigned to the ν(N-O)asym stretch.

The spectra of the ^{14}NO-^{15}NO mixture provides additional evidence for equivalent nitric oxide ligands in a dinitrosyl complex. Statistically the nitrosyl complex should exist as 25% $[Co(^{14}NO)_2]^{2+}$, 25% $[Co(^{15}NO)_2]^{2+}$, and 50% $[Co(^{14}NO)(^{15}NO)]^{2+}$. The bands corresponding to the $[Co(^{14}NO)_2]^{2+}$ and $[Co(^{15}NO)_2]^{2+}$ complexes can readily be seen to coincide with bands and shoulders at 1830, 1910 cm^{-1} and 1800, 1880 cm^{-1}, respectively. Assuming a nonlinear Y-X-Y molecule the frequencies of the bands for $[Co(^{14}NO)(^{15}NO)]^{2+}$ were calculated[16] and were found to be within 3 cm^{-1} of the strongest bands at 1810 and 1900 cm^{-1}.

If each NO molecule is treated as a dipole vector, the dipole vector for the entire vibrational mode can be taken to be the vector sum of these individual vectors. Since the in-

Table I. Assignment of Infrared Bands

Gas adsorbed	Wave number (cm^{-1})	Rel intens	Assignment
^{14}NO	1910	m	^{14}N–O antisym stretch of $[Co(NO)_2]^{2+}$
	1830	s	^{14}N–O sym stretch of $[Co(NO)_2]^{2+}$
^{14}NO, NH_3	2240	m	$^{14}N_2O$ stretch
	1880	m	^{14}N–O antisym stretch of $[Co(NH_3)(NO)_2]^{2+}$
	1800	s	^{14}N–O sym stretch of $[Co(NH_3)(NO)_2]^{2+}$
	1710	s	$(N-O)^-$ stretch of $[Co^{III}(NH_3)_nNO]^{2+}$
	1640	vs	$^{14}NH_3$ antisym deformation
	1520	m	ONO stretch of $[Co(ONO)]^{2+}$
	1430	vs	$^{14}NO_2$ antisym def of $[Co(NH_3)_nNO_2]^{2+}$
	1330	vs	$^{14}NO_2$ sym def of $[Co(NH_3)_nNO_2]^{2+}$
^{15}NO	1880	m	^{15}N–O antisym str of $[Co(NO)_2]^{2+}$
	1800	s	^{15}N–O sym str of $[Co(NO)_2]^{2+}$
^{15}NO, ND_3	2180	m	$^{15}N_2O$ stretch
	1850	m	^{15}N–O antisym str of $[Co(NH_3)(NO)_2]^{2+}$
	1770	s	^{15}N–O sym str of $[Co(NH_3)(NO)_2]^{2+}$
	1680	s	$(^{15}NO)^-$ stretch of $[Co^{III}(NH_3)_nNO]^{2+}$
	1490	m	$O^{15}NO$ stretch of $[Co(ONO)]^{2+}$
	1400	s	$^{15}NO_2$ antisym def of $[Co(NH_3)_n(NO_2)]^{2+}$
	1300	s	$^{15}NO_2$ sym def of $[Co(NH_3)_n(NO_2)]^{2+}$

tensities are proportional to the square of the gradient of the dipolar vectors, it is possible to approximate the angle between the two NO ligands by the formula[17]

$$\phi = 2\sqrt{\text{arccotan } R(\text{sym})/R(\text{asym})}$$

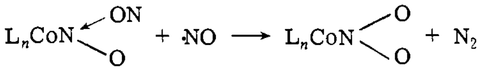
where ϕ is the ON–Co–NO bond angle and R is the intensity of the particular vibrational mode. Here, it is assumed that the Co–N–O linkage is linear. For $[Co(NO)_2]^{2+}$ in a Y-type zeolite, $R(\text{sym})/R(\text{asym}) = 0.310$, which indicates that ϕ is 123°.

Since the frequency of the N–O stretching vibration appears at a point only slightly below that of free NO, little or no back-donation with electron flow from the metal atom to the nitrosyl ligand is taking place. This is to be expected since no electron donors are coordinated to the cobalt ion, thus increasing the electron density on the metal ion.

Upon exposure of the CoY zeolite to ammonia and prolonged evacuation it appears that a $[Co(NH_3)]^{2+}$ complex is formed. This also reacts with NO, yielding a complex with two nitrosyl ligands per cobalt ion. The ir bands at 1800 and 1880 cm^{-1} are assigned to this complex. The 30 wave number shift between this complex and the previous dinitrosyl complex is attributed to the increase of electron density on the nitrosyl ligand, which is ultimately derived from the nonbonding pair of electrons on ammonia. The relative intensities of the two ir bands again indicates an ON–Co–NO bond angle of 123°. We propose that the complex is similar to that described in Figure 6, where the cobalt is coordinated to two nitrosyl ligands, one ammonia ligand and three oxide ions of the zeolite lattice.

Although the pentaamminenitrosylcobalt complex has been studied in detail, all previous work has been carried out in solution.[18,19] The 1710-cm^{-1} band falls within the range assigned to the NO^- stretching vibration. Previous work on the $[Co(NH_3)_5NO]^{2+}$ complex in solution, however, has shown that the NO^- vibrational mode in this complex falls between 1620 and 1647 cm^{-1} depending upon the anion. The much higher value of 1710 cm^{-1} observed in this study could be caused by two factors. Either the cobalt ions in the zeolite are coordinated with only four NH_3 ligands and the sixth coordination site is occupied by the zeolite or the cobalt ion is coordinated with five ammine ligands but the oxide ions in the second coordination sphere have a sufficiently strong interaction with the Co^{3+} ion to cause the 60–80 wave number shift that is observed. In view of the stoichiometry observed in homogeneous media we favor the latter interpretation; although the exact number of ammonia ligands has not been proven. The infrared frequencies and assignments for the nitrosyl complexes are summarized in Table I.

The disappearance of the band at 1710 cm^{-1} coupled with the appearance of ir bands corresponding to N_2O and NO_2^- suggests that a disproportionation reaction is taking place. Gwost and Caulton[8] have chosen to interpret this reaction as the oxidation of coordinated nitric oxide by free nitric oxide. This reaction has been observed in previous studies.[9] NaY and CoY zeolites have been observed to catalyze this reaction, although for NaY a temperature of −78° or less was required for the reaction. The reaction was not observed for the COY zeolites at 25°. For the cobalt nitrosyl complexes the proposed mechanism for this reaction involves the attack of the free NO on complexed NO^-.[8] The bent form of NO^- has a lone pair of electrons accessible to attack by the oxygen atom of the free NO. The reaction of a second free NO produces NO_2^- and N_2O. The observation that low pressures of NO (<10 Torr) over the $[Co^{III}(NH_3)_nNO]^{2+}$ complex failed to produce any N_2O lends support to this proposed mechanism.



$$L_nCoN\genfrac{}{}{0pt}{}{\swarrow ON}{\diagdown O} + \cdot NO \longrightarrow L_nCoN\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O} + N_2O$$

Even at low pressures of NO the intramolecular reaction of the $[Co(NH_3)_nNO]^{2+}$ complex to form N_2 and H_2O is significant. With the use of ^{15}NO, it was found that NH_3 and ^{15}NO reacted to form $^{15}N^{14}N$. This reaction readily occurs on a supported platinum catalyst at elevated temperatures;[20] however, it has not been previously reported for conventional nitrosyl complexes at room temperature. Feltham and coworkers[21] have studied the reaction of nitrosyl ruthenium complexes with amines but achieved no observable results with NH_3. Stronger amines such as NH_2OH produced the $(L_nRuN{\equiv}N)^+$ complex after reacting with $[L_nRuNO]^{2+}$. The N–O stretching frequency reported for the nitrosyl ruthenium complex was 1876 cm^{-1} which suggests an NO^+ ligand. In the $[Co^{III}(NH_3)_nNO]^{2+}$ complex, the activity is attributed to the high electron density on the nitrosyl ligand.

Since the addition of a second volume of NO failed to produce a measurable reaction, the activity must be poisoned by one of the products. The strong bands assigned to

NO_2^- stretching vibrations in the $[Co(NH_3)_nNO_2]^{2+}$ complex indicate that the nitro ligand produced by the parallel disproportionation reaction prevents any further formation of the nitrosyl complexes. The nitro complex is destroyed only by heating the complex under vacuum to 200°, and these conditions are sufficient to destroy the ammine complex also. Although the reaction system cannot be considered catalytic at the higher nitric oxide pressures, the formation of the undesirable nitro ligands may be prevented by going to lower partial pressures of NO where the disproportionation reaction does not occur.

These results clearly show that the reactivity of nitric oxide coordinated to cobalt(II) can be greatly enhanced by forming complexes with strong bases. The presence of the $[Co^{III}(NH_3)_nNO]^{2+}$ in a zeolite appears to facilitate the intramolecular reaction between the nitrosyl and ammonia ligands. This illustrates the unique function of zeolites as solvents.

Acknowledgment. The authors wish to acknowledge the support of this work by The Robert A. Welch Foundation under Grant No. A-257.

References and Notes

(1) C. C. Chao and J. H. Lunsford, *J. Phys. Chem.*, **76**, 1546 (1972).
(2) Y. Y. Huang, *J. Catal.*, **32**, 482 (1974).
(3) J. W. Jermyn, T. J. Johnson, E. F. Vansant, and J. H. Lunsford, *J. Phys. Chem.*, **77**, 2964 (1973).
(4) C. Naccache and Y. Ben Taarit, *Trans. Faraday Soc.*, **2**, 1475 (1973).
(5) C. C. Chao and J. H. Lunsford, *J. Phys. Chem.*, **78**, 1174 (1974).
(6) J. B. Peri, *J. Phys. Chem.*, **78**, 588 (1974).
(7) P. Finn and W. Jolly, *Inorg. Chem.*, **11**, 893 (1972).
(8) D. Gwost and K. G. Caulton, *Inorg. Chem.*, **13**, 414 (1974).
(9) P. Gans, *J. Chem. Soc. A*, 943 (1967).
(10) (a) E. F. Vansant and J. H. Lunsford, *J. Chem. Soc., Chem. Commun.*, 830 (1972); (b) *Trans. Faraday Soc.*, **69**, 1028 (1973).
(11) E. F. Vansant, Thesis for the Agregate of Higher Education, University of Antwerp, Antwerp, Belgium, 1974.
(12) E. F. Vansant and J. H. Lunsford, *Advan. Chem. Ser.*, **No. 121**, 441 (1973).
(13) R. Howe and J. H. Lunsford, to be submitted for publication.
(14) C. C. Chao and J. H. Lunsford, *J. Amer. Chem. Soc.*, **93**, 71 (1971).
(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N.Y., 1963.
(16) S. Pinchas and I. Laulicht, "Infrared Spectra of Labeled Compounds," Academic Press, London, 1972, p 28.
(17) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed., Interscience, New York, N.Y., 1972, p 696; (b) W. Beck, A. Melnikoff, and R. Stahl, *Chem. Ber.*, **99**, 3721 (1966).
(18) J. B. Raynor, *J. Chem. Soc.*, 997 (1966).
(19) P. Gans, *Chem. Commun.*, 144 (1965).
(20) K. Otto, M. Shelef, and J. T. Kummer, *J. Phys. Chem.*, **74**, 2690 (1970).
(21) P. G. Douglas and R. D. Feltham, *J. Amer. Chem. Soc.*, **94**, 5254 (1972).

Mechanism of Formation of (α,β) Unsaturated Aldehyde- and Ketone-Iron Tricarbonyl Complexes from the Corresponding Iron-Tetracarbonyl Complexes

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Abstract: The kinetics of the reaction:

$$(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4 \rightarrow \alpha(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3 + (1-\alpha)Fe(CO)_5 + (1-\alpha)C_6H_5CH{=}CHCOR + (2\alpha-1)CO \quad (1)$$

where R = H, CH_3, and C_6H_5 and α is the fraction of chelate complex $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3$ *per* mole of reagent complex, has been followed. The reaction is first order with respect to $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$, and the first-order rate constants (k_c) decrease with increase in concentration of $C_6H_5CH{=}CHCOR$ and are a function of CO concentration. $(1-\alpha)/\alpha$ changes linearly with $1/[C_6H_5CH{=}CHCOR]$ and also changes with CO pressure according to a square law. The results exclude an intramolecular chelation mechanism. A mechanism involving $Fe(CO)_3$ intermediate, which is responsible for the formation of the chelate complex, is suggested.

Many (π-*cis*-1,3-diene)$Fe(CO)_3$ complexes have been described in the literature,[1] since the preparation of (π-1,3-butadiene)$Fe(CO)_3$.[2] The nature of the iron-diene ligand bond has stimulated much interest from both theoretical and structural viewpoints.[3,4] Recently some π-hetero-1,3-diene complexes of iron carbonyl have also been described in which the heteroatom is oxygen[5] or nitrogen.[6] These complexes also have a structure similar to that of (π-*cis*-1,3-diene)$Fe(CO)_3$ complexes, with heteroatom lone pairs which do not participate in bonding to the iron.[7]

The iron atom is unique in its inclination to coordinate 1,3-diene or 1,3-heterodiene planar ligands.[1] This may depend both on the high stability of such structures and/or on the particular reaction mechanism involved. In order to clarify this mechanism a kinetic study of the formation reaction was undertaken. These complexes are obtained by photochemical reaction between the diene ligand and $Fe(CO)_5$[8] or by thermal reaction between the diene and $Fe_2(CO)_9$.[6]

In both methods of preparation, the percursor of the (π-diene)$Fe(CO)_3$ is the corresponding (π-diene)$Fe(CO)_4$ complex. However, since the $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$ and $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3$ are more stable than the corresponding (π-diene) complexes, the reaction studied kinetically is the formation of $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_3$ from the corresponding $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$ (with R = H, CH_3, C_6H_5).

For the reaction with R = H, literature reports[9] suggest the following stoichiometry

$$2(\pi\text{-}C_6H_5CH{=}CHCHO)Fe(CO)_4 \longrightarrow (\pi\text{-}C_6H_5CH{=}CHCHO)Fe(CO)_3 + Fe(CO)_5 + C_6H_5CH{=}CHCHO$$

but no mention was made of possible reaction mechanisms.

Recently, other authors[6] have assumed an internal chelation mechanism on the basis of the different reactivity of the complexes $(\pi\text{-}C_6H_5CH{=}CHCOR)Fe(CO)_4$ in the two forms, s-cis and s-trans.