reaction of elemental sodium and tellurium, and its presence is responsible for the yellow solution that precedes the precipitation of Na_2Te. Na_2Te is either insoluble in liquid ammonia or does not absorb in the spectral region 220–700 nm. No polytelluride higher than Na_2Te_3 is formed under the conditions of this investigation.

Acknowledgment. Portions of this data were obtained by Dale Drueckhammer and Jerry Springs, currently at Texas A&M University, and Michael Re and Mary Alice Schaefer, currently at Texas Christian University. We gratefully acknowledge the financial support of The Robert A. Welch Foundation and the Tarleton State University Organized Research Fund.

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Oxidation of 2-Propanol over Cobalt–Y Zeolites

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Cobalt–dinitrosyl complexes in zeolite Y may be oxidized with O_2, albeit rather slowly, to the corresponding nitro and nitrito complexes. In the absence of weakly adsorbed NO, the rate of oxidation is strongly inhibited by the presence of other ligands such as acetone. As an alternative, the nitro and nitrito complexes may be formed directly by reacting the Co–Y zeolite with NO_2. Both the nitro and nitrito complexes react with 2-propanol to form acetone and the dinitrosyl complexes. In a flow reactor at 70 °C this reaction occurs with high selectivity to acetone, but the turnover number is ca. 2.5, which suggests that the reaction is stoichiometric rather than catalytic. Thus, the potential utilization of cobalt–dinitrosyl complexes in zeolites for the catalytic activation of O_2 is limited by the rate at which the dinitrosyl complexes can be oxidized.

Introduction

The utilization of transition-metal complexes to activate molecular oxygen for the catalytic oxidation of organic substrates via a nonradical mechanism has been the subject of intense investigation over the past two decades. Tovrog, Diamond, Mares, and co-workers,[1–6] as well as Andrews and co-workers,[7–9] have found that certain metal–nitro complexes are effective as intermediates in a variety of oxidation reactions, including oxygen atom transfer to alkenes. Solar et al.[10] have recently reviewed the literature in this field. Catalytic cycles generally involve the oxidation of a bent mononitrosyl ligand to a nitrogen-bound nitro complex, which is capable of oxidizing the organic substrate, and in the process the nitrosyl ligand is re-formed. The oxygen-bound nitro and nitrito ligands were not nearly so effective in the systems that have been studied. (Here we adopt the convention of referring to the oxygen-bound bidentate complex as a chelating nitro complex.[11])

Previous work in our laboratory has demonstrated that cobalt–dinitrosyl complexes may be formed in zeolite Y, and these complexes are intermediates in the catalytic reduction of nitric oxide by ammonia.[12–14] The cobalt(II) apparently was coordinated to two or three oxygen atoms of the zeolite framework, in addition to the nitrosyl ligands. The nitrosyl ligands were oxidized with O_2 at 25 °C, albeit the reaction was rather slow with a half-life on the order of several hours. Following oxidation, a new infrared band at 1520 cm^{-1} suggested that a nitrito complex was formed.[12]

Table I. N–O Stretching Bands of Cobalt–Dinitrosyl Complexes in Zeolite Y

complex[a]	ν_s, cm^{-1}	ν_a, cm^{-1}	R_s/R_a[b]	ϕ, deg[c]
$[Co(NO)_2]^{2+}$	1902	1818	0.48	111
$[(H_2O)Co(NO)_2]^{2+}$	1895	1814	0.23	129
$[(mixed)Co(NO)_2]^{2+}$	1886	1798	0.25	127
$[(C_3H_6O)Co(NO)_2]^{2+}$	1894	1803	0.34	120
$[(C_3H_6O)_nCo(NO)_2]^{2+}$	1890	1795	0.31	122
$[(2\text{-PrOD})Co(NO)_2]^{2+}$	1895	1797	0.40	115
$[(2\text{-PrOD})_nCo(NO)_2]^{2+}$	1891	1796	0.31	122
$[(NH_3)Co(NO)_2]^{2+}$	1878	1798	0.57	106
$[(NH_3)_nCo(NO)_2]^{2+}$	1872	1789	0.31	122

[a] The exact number of ligands, other than NO, is unknown. It is assumed that after extensive evacuation one ligand remains and after brief evacuation *n* ligands remain. [b] Intensity ratio of symmetric asymmetric bands. [c] ON–Co–NO bond angle.

The present study was carried out to determine whether these cobalt–dinitrosyl complexes in zeolite Y could be used as a starting point for the catalytic oxidation of 2-propanol to acetone, in a manner analogous to the use of cobalt–mononitrosyl complexes as homogeneous oxidation catalysts. It will turn out (see below) that the similarities between the two systems are not extensive, and in the zeolite a catalytic cycle is impeded by the slow reoxidation of a modified dinitrosyl complex. Moreover, the organic substrate appears to be oxidized in the zeolite by nitrito ligands, as well as by nitrogen-bound nitro ligands.

Experimental Section

The Co–Y zeolites were obtained by aqueous-ion exchange of a Na–Y zeolite supplied by Linde Co. (Lot No. Y-52 3365-94). Most of the results were obtained on a Co–Y zeolite that contained 14 Co(II) ions per unit cell; however, another sample that contained 2.8 ions per unit cell was also used to determine turnover numbers (TON). The zeolites were dehydrated by heating slowly to 400 °C, either under vacuum for spectroscopic studies or in flowing He for catalytic studies.

The CP grade NO obtained from Matheson contained NO_2, which was formed by the disproportionation of NO. The NO_2 was removed for spectroscopic studies by repeated distillation from a vessel at 138 K (cooled by pentane slush) to one at 77 K. For catalytic studies the NO

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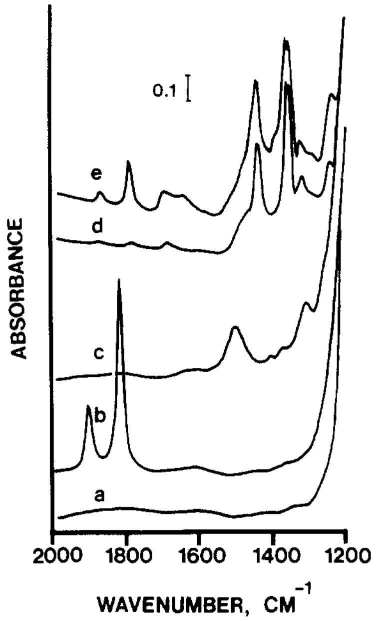

Figure 1. Infrared spectra of cobalt complexes in zeolite Y: (a) background spectrum; (b) spectrum after addition of 40 Torr of NO for 5 h, followed by evacuation of the gas phase for 30 s; (c) spectrum after addition of 95 Torr of O_2 for 4 h; (d) spectrum of sample as in (c) after addition of 5 Torr of 2-propanol overnight; (e) spectrum after 2 h at 70 °C. All reactions were carried out at room temperature.

was passed through a trap at 138 K. Ultrahigh-purity O_2, also obtained from Matheson, was used without further purification. Research grade 2-propanol (Fisher Scientific) and 2-propanol-*d* of 99.1 atom % D (MSD Isotopes) were used after dehydrating with a 3-Å molecular sieve.

Infrared spectra were recorded by using a Perkin-Elmer 580B spectrophotometer. The infrared cell has been described previously.[15] Zeolite samples in the form of thin, self-supporting wafers (ca. 7 mg/cm^2) were degassed and further treated in one section of the cell and then lowered between KCl windows for recording spectra.

Diffuse-reflectance spectra were obtained by using a Varian 2300 spectrophotometer, with $BaSO_4$ as a reference. The sample cell was a quartz cuvette attached to a Pyrex section where the zeolite was pretreated. Spectra in the region 300–800 nm were recorded, processed, and plotted as the logarithm of the Schuster–Kubelka–Munk remission function vs. wavelength.

The oxidation of 2-propanol was followed by using a continuous-flow microreactor system that included an on-line sampling valve. The reactor was a 4.4 mm i.d. Pyrex glass tube, 250 mm in length, that contained 0.2 g of Co–Y zeolite. The 2-propanol was injected with a Sage microsyringe pump. Gases were analyzed by using a 10 ft × $^1/_8$ in. stainless-steel column that was packed with 10% Carbowax 20 M on Chromasorb W (80–100 mesh).

The typical reaction scheme involved (1) cooling the degassed zeolite to the reaction temperature, (2) passing 2-propanol over the catalyst until breakthrough occurred, (3) flowing a 2-propanol–NO–O_2 mixture over the catalyst for 10 min, and (4) stopping the NO flow and then flowing a 2-propanol–O_2 mixture over the catalyst. Variations on this scheme will be described in the subsequent section.

Results

Infrared Studies. As previously observed,[12-14] adsorption of NO by a dehydrated Co–Y zeolite gives rise to a pair of infrared bands that are at 1818 and 1902 cm^{-1} (Figure 1b). Shoulders at 1800 and 1890 cm^{-1} were observed in the presence of gas-phase NO or upon short evacuation (30 s). On the basis of their thermal stability and ^{14}NO–^{15}NO spectra, these bands have been assigned to cobalt–dinitrosyl complexes in the zeolite.[12] The exact position and relative intensity of the bands given in Table I depend upon the presence or absence of other ligands in the complex (i.e. ligands other than the framework oxygen atoms). For example, strongly coordinated NH_3 induces a 25–30-cm^{-1} red shift in both bands. This coordinated ammonia is unreactive, which suggests that it is trans to the NO ligands and is inside the small cavities of the zeolite.[12] The ligands labeled "mixed" refer to those that are present after oxidation with O_2 and subsequent reduction with 2-propanol. The complexes probably contain acetone, 2-propanol, and water as ligands.

Table II. Rate Constants for the Oxidation of Cobalt–Dinitrosyl Complexes in Zeolite Y

complexes	evacuation time, min	oxygen press., Torr	oxidn temp, °C	10^2k, min^{-1}
$[Co(NO)_2]^{2+}$	0.5	95	25	9.60
	0.5	50	25	8.45
	0.5	10	25	1.87
	10	95	25	2.57
$[(C_3H_6O)_nCo(NO)_2]^{2+}$	0.5	95	25	1.61
	10	95	25	<0.1
	10	95	70	3.83
$[(mixed)Co(NO)_2]^{2+}$		95	70	3.74
		95	25	<0.1
$[(C_3H_6O)Co(NO)_2]^{2+}$	0.5	95	25	>35
	10	95	25	<0.1
$[(H_2O)Co(NO)_2]^{2+}$	0.5	95	25	>35
$[(2\text{-}PrOD)Co(NO)_2]^{2+}$	0.5	95	25	>35

The addition of water, 2-propanol, or acetone likewise causes a shift in wavenumber of the dinitrosyl bands, as well as a change in the intensity ratio, R_s/R_a. As indicated in Table I, the extent of the shift is greatest in the case of acetone. It is possible to approximate the ON–Co–NO bond angle by eq 1, assuming that

$$\phi = 2 \text{ arccot } (R_s/R_a)^{1/2} \qquad (1)$$

the Co–N–O linkage is linear.[16] From the calculated bond angles given in Table I it is evident that the presence of water, 2-propanol, acetone, or excess ammonia increases ϕ, but small amounts of ammonia cause ϕ to decrease. The rather large change in ν and ϕ suggests that all of the ligands become coordinated to the cobalt. Only ammonia and water are small enough to enter through the 2.2-Å aperture to the small cavities and coordinate in the trans position. Here we assume that the cobalt ions that give rise to these complexes are located in a site II position in the zeolite, which is on the sixfold axis of the small cavity but extended slightly into the large cavity.[14]

The rate at which the dinitrosyl complexes are oxidized, as determined from the disappearance of ν(NO) in the IR spectra, is influenced by a number of factors including the O_2 pressure, temperature, the presence or absence of other ligands, and even the length of time the sample has been under vacuum after adding the NO to form the complex. The rate was first order with respect to the concentration of dinitrosyl complexes, and the corresponding rate constants obtained for several conditions are given in Table II. It appears that weakly coordinated NO that is oxidized to NO_2 may promote the further oxidation of the nitrosyl ligands. Moreover, in the absence of weakly coordinated NO, acetone impedes the oxidation process at 25 °C, perhaps by preventing the coordination of oxygen with the cobalt. Likewise, oxidation of the $[(mixed)Co(NO)_2]^{2+}$ complex is relatively slow, even at 70 °C. This result has serious implications with respect to the catalytic reaction, which will be described subsequently.

When O_2 was added after 30-s evacuation of the gas-phase NO, a rather broad band appeared at 1505 cm^{-1} (probably the same band reported previously at 1520 cm^{-1}),[12] and an additional band was observed at 1320 cm^{-1} with a shoulder at 1270 cm^{-1} (Figure 1c). The band at 1270 cm^{-1} became more distinct when the NO was evacuated for 10 min before adding the O_2. The band at 1505 cm^{-1} was attributed to ν(N=O) of a nitrito ligand. As will be subsequently shown, adsorption of NO_2 in the Co–Y zeolite also gives rise to this band. The bands at 1270 and 1320 cm^{-1} disappear at different rates upon reaction with 2-propanol (see below); therefore, they must result from different species. For reasons to be discussed, these two bands are attributed to chelating and nitrogen-bound nitro ligands, respectively.

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Table III. Infrared Band Assignments

wavenumber, cm^{-1}	intensity	assignment
1902	vs	N-O asym str in $[Co(NO)_2]^{2+}$
1818	vs	N-O sym str in $[Co(NO)_2]^{2+}$
1700	vs	C=O str of acetone
1670-1720	vs	C=O str of acetone coordinated with cobalt(II) ion in zeolite Y
1640	m	zeolitic water
1505	vs	N=O str of nitrito ligand in $[Co(ONO)_2]^{2+}$
1460	s	CH_3 asym def of 2-propanol
1420	s	CH_3 asym def of acetone
1388, 1378	s	doublet: CH_3 sym def of 2-propanol due to in-plane and out-of-plane bend of two methyl groups in 2-propanol
1367	s	CH_3 sym def of acetone
1350	s	in-plane O-H def of 2-propanol
1320	m	N-O asym str of N-bound nitro ligand in $[Co(NO_2)_2]^{2+}$
1270	m	N-O asym str of chelating nitro ligand in $[Co(NO_2)_2]^{2+}$
1231	s	C-C-C str and bend in the C-C(O)-C group in acetone

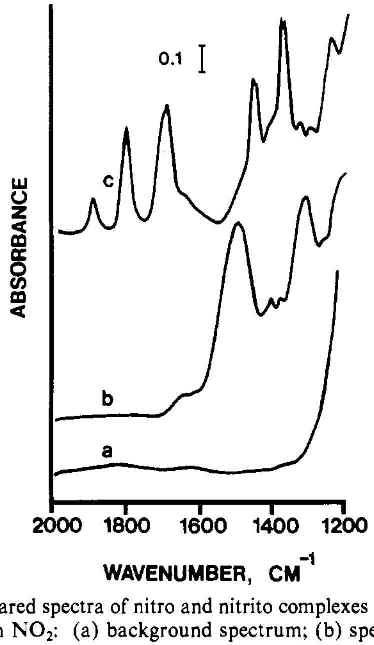

Figure 2. Infrared spectra of nitro and nitrito complexes in Co-Y zeolite prepared from NO_2: (a) background spectrum; (b) spectrum after simultaneous addition of 40 Torr of NO and 95 Torr of O_2 for 30 min at 25 °C and evacuation of gas-phase NO_2 for 30 s at 25 °C; (c) spectrum 30 min after addition of 5 Torr of 2-propanol-*d* at 25 °C.

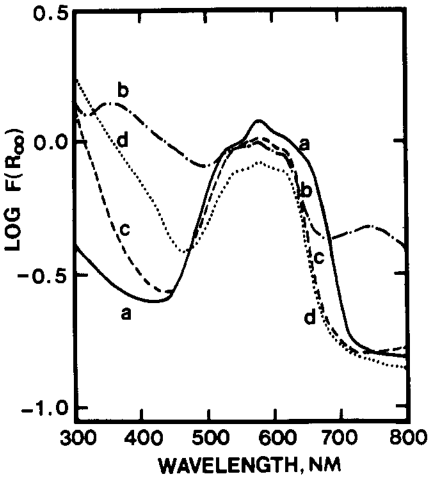

Figure 3. Diffuse-reflectance spectra of a Co-Y zeolite: (a) spectrum of sample dehydrated at 673 K; (b) spectrum after addition of 40 Torr of NO for 5 h, followed by evacuation of the gas phase for 30 s; (c) spectrum after addition of 95 Torr of O_2 for 4 h; (d) spectrum after addition of 20 Torr of 2-propanol overnight. All reactions were carried out at room temperature.

Upon addition of 2-propanol-*d* to the oxidized zeolite wafer having bands at 1505, 1320, and 1270 cm^{-1}, new bands rapidly appeared at 1886, 1798, 1700, 1720, 1460, 1420, 1388, 1378, 1367, 1350, and 1231 cm^{-1}, as shown in Figure 1d. In a separate experiment (spectra not shown) it was confirmed that the bands at 1700 and 1720 cm^{-1} are due to the C=O stretching modes of acetone, part of which is coordinated to Co, and the remaining bands are due to 2-propanol and acetone in the zeolite, for which the detailed assignments are given in Table III. These results indicate that 2-propanol was partially oxidized to acetone with the concomitant reduction of the nitrito and perhaps some nitro ligands back to nitrosyl ligands. From a comparison of parts d and e of Figure 1 it is evident that the extent of these reactions increases with increasing temperature. The dinitrosyl bands, however, never return to their original intensity, even upon the addition of pure NO.

These results may be compared with those of a similar experiment in which the excess NO was completely removed before the first addition of O_2. In this case, 4 h in 95 Torr of O_2 at room temperature was required to oxidize the nitrosyl ligands. There were almost no nitrito complexes, although the spectra of the nitro complexes (1270 and 1320 cm^{-1}) were clearly evident. The oxidation of 2-propanol-*d* was slow in this sample, and even after 18 h at room temperature only a relatively small amount of acetone and cobalt dinitrosyl complex was detected by infrared spectroscopy.

For comparison it is instructive to consider the results obtained upon adding a mixture of NO and O_2 to the Co-Y zeolite. The two gases reacted rapidly to form NO_2. The spectrum of Figure 2b, obtained after 30-s evacuation of the gas phase, indicates that again the nitrito and nitro ligands were present in the sample. The concentration of nitrito complexes was approximately 10-fold greater in this sample, compared to that in the sample prepared by adding NO and O_2 separately. The oxidation of 2-propanol-*d* was facile, and the formation of acetone was accompanied by the formation of the dinitrosyl complex. Similar results were obtained when pure NO, rather than a mixture of NO and O_2, was added to the zeolite.

Diffuse-Reflectance Studies. The diffuse-reflectance spectrum of Figure 3a exhibits bands at 545, 575, and 610 nm, which are characteristic of Co(II) ions in distorted tetrahedral symmetry.[17,18] Upon addition of NO to the sample there was a 10% reduction in intensity of the tetrahedral Co(II) spectrum, and new bands were observed at 360 and 745 nm, as shown in Figure 3b. The relative increase of absorbance in the 300-500-nm region was previously noted, although distinct bands were not resolved.[14] In view of the infrared results we attribute both bands to the dinitrosyl complex. The rather modest decrease in the tetrahedral Co(II) spectrum indicates that under these conditions only about 10% of the cobalt ions are forming the dinitrosyl complex.

When O_2 was added to the sample, the absorbance in the 350-450-nm region decreased markedly, and the band at 750 nm disappeared (Figure 3c). The latter band previously was attributed to the photoinduced oxidation of Co(II) to Co(III),[14] but the current results suggest that it probably is also part of the cobalt dinitrosyl manifold. Finally, upon overnight exposure to 2-propanol the absorbance in the 350-450-nm region increased (Figure 3d), but there is no clear evidence for the dinitrosyl bands. This is consistent with the infrared results, as the number of nitrosyl complexes re-formed by this treatment is expected to be small. The decrease in the bands at 545, 575, and 610 nm suggests additional complexation of the tetrahedral Co(II) with 2-propanol and acetone.

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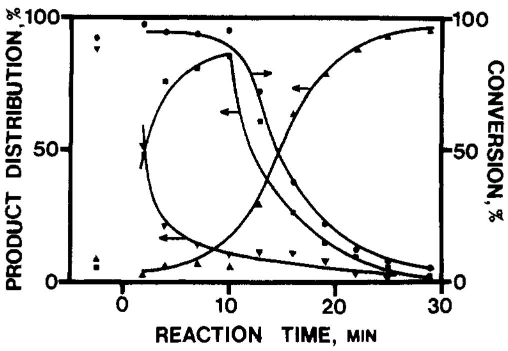


Figure 4. Product distribution and 2-propanol conversion in a flow reactor (0.2 g of Co–Y zeolite, $T = 70$ °C): (●) conversion; (▼) CO_2; (■) acetone; (▲) 2-propanol. Total flow rate = 56 mL/min. The catalyst was exposed to a mixture of NO, O_2, and 2-propanol for 10 min; then at $t = 0$, NO was deleted from the gas stream.

Reaction Studies. With the use of the reaction sequence described in the Experimental Section, the data depicted in Figure 4 were obtained. During the period when NO (70 Torr), O_2 (200 Torr), and 2-propanol (14 Torr) were passed over the catalyst at a flow rate of 56 mL/min and a temperature of 343 K, the conversion was 90%, but the selectivity to CO_2 was 87%. After the NO flow was stopped, but with the flow of 2-propanol (14 Torr) and O_2 (200 Torr) continued, the 2-propanol conversion increased to 95% and the selectivity to acetone increased over a period of 10 min to 85%. However, after 10 min the conversion to acetone began to decrease rapidly. A comparison of the integrated amount of acetone relative to the cobalt ions in the zeolite revealed a TON = 2.5 acetone molecules/Co(II) atom. The TON was essentially the same for zeolites containing 2.8 and 14 cobalt atoms and for zeolites that had been regenerated by again passing a NO plus O_2 mixture over the catalyst.

The maximum rate achieved under conditions of high acetone selectivity was 12×10^{-3} mol/(h g of catalyst) for the Co–Y zeolite. Under the same conditions (70 °C, 56 mL/min) and typical reaction scheme outlined in the Experimental Section, a Na–Y zeolite promoted a reaction rate of 2.5×10^{-3} mol/(h g of catalyst). Apparently a small amount of NO_2 remained in the Na–Y zeolite and was effective in oxidizing the 2-propanol. Without the NO treatment, the Co–Y zeolite exhibited no activity for 2-propanol oxidation at temperatures less than 100 °C.

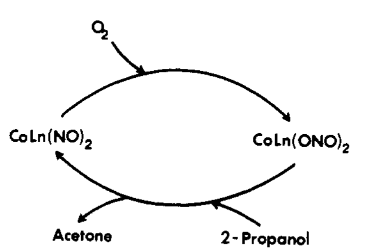
A similar experiment was carried out in which a mixture of purified NO (70 Torr) and 2-propanol (14 Torr) was passed over the catalyst; then the NO was replaced by O_2 (200 Torr). In this case, the TON was 0.2, which is approximately one-tenth the value obtained following oxidation of the catalyst with NO_2 via NO + O_2.

Discussion

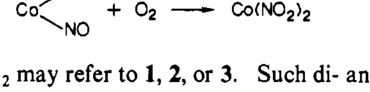
The oxidation of dinitrosyl ligands, although slow in certain cases (Table II), is evident from the infrared results of Figure 1. The assignment of the band at 1505 cm^{-1} to $\nu(N{=}O)$ is reasonably straightforward, as several known nitrito complexes, including $[Co(NH_3)_5(ONO)]Cl_2$, exhibit IR bands from this mode in the 1450–1485-cm^{-1} region.[11] The $\nu(N{-}O)$ mode typically absorbs in the 1050–1100-cm^{-1} region, which is opaque in the zeolite samples because of absorption by the framework.

There is some ambiguity, however, as to whether the bands at 1270 and 1320 cm^{-1} should be assigned to nitrogen-bound or chelating, oxygen-bound nitro complexes. Both types of ligands have ν_a bands in the 1250–1490-cm^{-1} region with ν_s bands in the 1190–1330-cm^{-1} region.[11] There appears to be a direct correlation between the value of ν_a and ν_s; the separation between the two bands is >50 cm^{-1}. The bands at 1270 and 1320 cm^{-1} in the zeolite are consistent with ν_a of two different nitro species, but from the available IR data it does not appear possible to distinguish between the two possible forms. On the basis of differences in reactivity, knowing that the nitrogen-bound species tends to be more reactive, we assign the 1320-cm^{-1} band to that form and the 1270-cm^{-1} band to the chelating nitro complex.

Scheme I

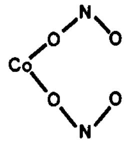


When oxidation of the dinitrosyl is with O_2, one may write a straightforward reaction



$$Co\begin{smallmatrix}NO\\NO\end{smallmatrix} + O_2 \longrightarrow Co(NO_2)_2 \qquad (2)$$

where $Co(NO_2)_2$ may refer to **1**, **2**, or **3**. Such di- and polynitro



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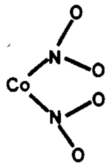
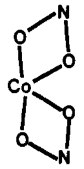


2

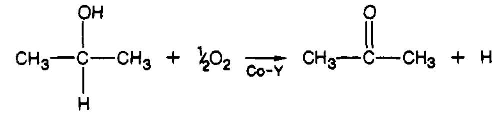
or



3

and nitrito complexes are well-known in inorganic chemistry. The observed TON of ca. 2.5 apparently results from the stoichiometric oxidation of 2-propanol by these complexes.

In an attempt to construct a catalytic cycle for reaction 3 over $[Co^{II}(NO)_2]Y$ zeolites, it becomes evident from the infrared spectra and overall reaction data that the slow step in the series of reactions in Scheme I is the oxidation of the dinitrosyl ligands to nitro and nitrito ligands. Once this oxidation step has taken place, the conversion of 2-propanol to acetone is facile and occurs even at room temperature (Figure 2) with the partial regeneration of the dinitrosyl complex.



$$CH_3{-}\underset{H}{\overset{OH}{C}}{-}CH_3 + \tfrac{1}{2}O_2 \xrightarrow[\text{Co-Y}]{} CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_2O \qquad (3)$$

The oxidation of cobalt mononitrosyl complexes with O_2 has been studied by Clarkson and Basolo,[19] who showed that the presence of nitrogen or phosphorus bases promoted the formation of nitro complexes. Complexes containing two nitrosyl ligands have not been successfully oxidized, except in zeolites, and even in this case the rate is slow unless weakly held NO is present. It is likely that this NO is converted to NO_2, which in turn is responsible for the oxidation of the nitrosyl ligands. In a separate experiment it was demonstrated that exposure of a $[Co^{II}(NO)_2]$-Y zeolite to NO_2 caused the dinitrosyl IR bands to disappear completely at room temperature with the concomitant formation of nitro and nitrito bands. Presumably the NO_2 oxidized, rather than simply displaced, the nitrosyl ligands. Nitrosyl oxidation mechanisms involving two metal cations, which have been suggested for homogeneous systems,[19] are unlikely in the zeolite where the complexes are relatively immobile. Moreover, the reaction was found to be first order with respect to the complex concentration.

Obviously, when NO and O_2 were simultaneously present in the catalytic flow experiments, NO_2 was produced, and the formation of nitro and nitrito ligands was rapid. Thus, the difficult problem of oxidizing nitrosyl ligands with O_2 was circumvented by having NO_2 present in the gas phase to form nitro and nitrito ligands directly. Uncoordinated NO_2, however, being a strong oxidant, effected the complete oxidation of 2-propanol to carbon dioxide. When NO was deleted from the gas mixture, the selective

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oxidation of 2-propanol occurred, but in a stoichiometric rather than a catalytic manner. A catalytic cycle is not possible, at least on the time scale employed here, because the reoxidation of the dinitrosyl complex designated $[(\text{mixed})\text{Co(NO)}_2]^{2+}$ is slow at 70 °C with O_2 as the oxidizing agent.

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Registry No. NO, 10102-43-9; NO_2, 10102-44-0; 2-propanol, 67-63-0; acetone, 67-64-1.

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Binuclear Platinum(II) Photochemistry. Reactions of Organometallic Hydrides with Electronically Excited Tetrakis(pyrophosphito)diplatinate(II)

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The $d\sigma^*p\sigma$ triplet excited state of $Pt_2(P_2O_5H_2)_4^{4-}$ (Pt_2) abstracts a hydrogen atom from R_3EH (E = Sn, Ge, Si; R = alkyl, phenyl) in acetonitrile solution. The rate constant for H atom transfer decreases according to Sn > Ge ≫ Si. The ultimate product of the reaction, Pt_2H_2, is thermally stable when generated from stannanes or germanes but it decomposes by secondary photoprocesses to H_2 and other Pt_2 complexes. In the case of Si, Pt_2H_2 reacts thermally with other species in the solution, regenerating Pt_2 and forming H_2. For E = Sn or Ge, another reaction product, $Pt_2(ER_3)_2$, is formed by the addition of $R_3E^{\bullet}$ to Pt_2. Each of these complexes is characterized by a very intense absorption band that is red-shifted with respect to that of Pt_2 (Bu_3Sn, 427 nm; Ph_3Ge, 430 nm) and each exhibits an intense broad emission (Sn, 527 nm; Ge, 531 nm). Photolysis of $Pt_2(ER_3)_2$ yields Pt_2 and $R_3E^{\bullet}$.

Introduction

The d^8–d^8 binuclear complexes (M_2: M = Rh, Ir, Pt) are known[2–7] to possess $d\sigma^*p\sigma$ triplet excited states ($^3M_2^*$) whose lifetimes are usually long enough to allow bimolecular photochemical reactions to take place. The electron-transfer reactions in which M_2 complexes act as one-electron excited-state reductants have been thoroughly investigated.[2,4–8] However, the M_2 complexes also possess two open axial coordination sites, which make them good candidates for excited-state atom-transfer reactions. This type of reactivity has not been systematically investigated, although a hydrogen atom transfer, $RH + {}^3M_2^* \rightarrow R^{\bullet} + {}^{\bullet}M_2H$, was proposed by Roundhill[9] to be a primary process in the Pt_2 photoassisted dehydrogenation of 2-propanol to acetone ($Pt_2 = Pt_2(P_2O_5H_2)_4^{4-}$). Recent work in our laboratory has provided support for Roundhill's proposal, and the key intermediate Pt_2H_2 has been characterized.[7,10] Our work also has revealed that excited M_2 complexes can activate other organic substrates, including hydrocarbons (e.g., toluene).[7] Because of its long lifetime (10 μs), high triplet energy (57.7 kcal mol^{-1}),[8,11] and stability, Pt_2 is well suited for photocatalysis.

It is important to explore the reactions of $^3Pt_2^*$ with bonds other than C–H and to understand its atom-transfer reactivity in more detail. For these reasons, the photochemical reactions of Pt_2 with a series of R_3EH (E = Sn, Ge, Si) molecules have been investigated. In the course of this work, some secondary reactions yielding unexpected products were discovered.

Results and Discussion

Reactions with Tributyltin Hydride. An acetonitrile solution of Pt_2 and Bu_3SnH (typically in 4–20-fold excess) turns yellow rapidly under nearly monochromatic 370-nm irradiation. Two products absorbing at 314 and 427 nm are formed (Figure 1). Both products are stable when the irradiation is interrupted.

The absorption band at 314 nm is attributable to Pt_2H_2. The ^{31}P NMR spectrum of Pt_2H_2 (Figure 2) exhibits a triplet (J(P,H) = 7.3 Hz) at δ = 27.9 with two satellites due to ^{31}P–^{195}Pt coupling: ^1J(P,Pt) = 2180 Hz. The absorption band at 314 nm disappears immediately upon exposure of the solution to air. When the solution containing the photoproducts is irradiated at 313 nm, the 314-nm absorption band decreases with concomitant increase of the Pt_2 absorption at 373 nm, whereas the 427-nm band remains unchanged. All these experiments clearly show that the reaction product absorbing at 314 nm is Pt_2H_2.[10]

The ^{31}P NMR spectrum of the 427 nm product (Figure 2) is characteristic of a symmetrical Pt_2X_2 species with equivalent phosphorus atoms. A single peak at 31.1 ppm is present with two small satellites corresponding to ^{31}P–$^{117,118}Sn$ coupling:[12] ^2J(P,Sn) = 69 Hz. Two other satellites are due to ^{31}P–^{195}Pt coupling: ^1J(P,Pt) = 2290 Hz. On the basis of this NMR spectrum, the photoproduct is formulated as $Pt_2(SnBu_3)_2$, with $SnBu_3$ groups coordinated to Pt_2 at axial positions (a Sn–Pt–Pt–Sn unit). The chemical shift and P–Pt coupling are at the upper limits of the ranges typical of axial $Pt^{III}{}_2X_2$ complexes ($18 < \delta < 31$; $2085 < {}^1J(\text{P,Pt}) < 2290$ Hz).[13–15]

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