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Bonding Character in Tetracoordinate (Phthalocyaninato)iron(II) Complexes with Electron-Withdrawing Substituents As Studied by Mössbauer Spectroscopy

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Received October 15, 1986

Mössbauer spectra of tetracoordinate (phthalocyaninato)iron(II) complexes with electron-withdrawing substituents were measured. Two kinds of bonding parameters, Σ and Π, were introduced for substituted phthalocyanines to interpret Mössbauer parameters in connection with the bonding characteristics of the macrocyclic ligands. They represent σ- and π-bonding properties, respectively, and are defined to be larger when more electron density is placed on the iron. Calculated orders of Σ and Π are in a good correlation with the sum of the Hammett σ constants, $\Sigma\sigma$, of the substituents. Several tetracoordinate (porphyrinato)iron(II) complexes were treated similarly.

Introduction

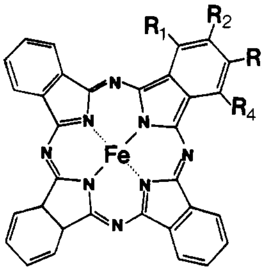
The electronic structure of the iron atom in (phthalocyaninato)- or (porphyrinato)iron(II) complexes is affected by both axial ligands and macrocyclic phthalocyaninato or porphyrinato ligands. Electronic effects are transmitted to and from various points on the macrocyclic ring through the σ and π bonds between the four nitrogens and the central iron. Substituents on the periphery of the macrocyclic ring have been shown to affect the physical and chemical properties of metalloporphyrins: redox potentials[1-4] of both macrocyclic ring and metal redox reactions, electronic spectra,[5,6] NMR shifts,[7-9] EPR parameters,[10] spin states[11] of the central metal atom, and rate[12,13] and equilibrium[14] constants for axial ligation. In some cases these physical properties have been shown to correlate with the Hammett σ constants.[15-17]

Recent studies have shown that there is a substantial cis effect between the macrocyclic ligands and the axial ligands: the macrocyclic ligands modify their σ- and π-bonding characteristics in order to accommodate the requirements of the axial ligands[18,19] and vice versa.[20] Thus, the intrinsic bonding characteristics of the macrocyclic ligands are difficult to be determined by studies of hexacoordinate (phthalocyaninato)- or (porphyrinato)iron complexes with the axial ligands, and we believe that tetracoordinate planar complexes are well suited for such studies.

Iron-57 Mössbauer parameters characterize electronic structure of iron complexes, since the isomer shift, δ, reflects the electron density at the iron nucleus, while the quadrupole splitting, ΔE_Q, is related to the electron distribution among the iron orbitals. In the present paper, Mössbauer data for tetracoordinate (phthalocyaninato)iron(II) complexes with electron-withdrawing substituents are given, and a new method for calculating the bonding parameters of macrocyclic ligands is discussed.

Experimental Section

Substituted (phthalocyaninato)iron(II) complexes **2**–**7** were prepared by both the "nitrile" and "anhydride" methods described previously.[6,21,22] All compounds gave satisfactory elemental analyses. Complexes **2**–**4** were synthesized as new compounds, and the preparations of **2** and **3** were reported elsewhere.[21] Complex **4** was synthesized as follows: 280 mg of (1,2,8,9,15,16,22,23-octacarboxyphthalocyaninato)iron[21] was refluxed in 10 mL of thionyl chloride for 20 h, and the excess thionyl chloride was removed on a rotary evaporator. The residue was a tetraanhydride of the starting compound (IR $\nu_{C=O}$ at 1720 cm^{-1}). Anal. Calcd for $C_{40}H_8N_8O_{12}Fe$: C, 56.63; H, 0.95; N, 13.21. Found: C, 56.99; H, 0.92; N, 13.33. This anhydride was reacted with a slight excess of decylamine in *N*-methyl-2-pyrrolidone at 70 °C for 5 h under nitrogen atmosphere, and the solution was diluted with benzene after cooling. The precipitate was collected and heated in vacuo at 200 °C for 12 h and then chromatographed on a basic alumina column with $CHCl_3$–MeOH as eluent. After the solid was dried in vacuo, 215 mg of dark blue product was obtained. Anal. Calcd for $C_{80}H_{92}N_{12}O_8Fe$: C, 68.36; H, 6.60; N, 11.96. Found: C, 68.18; H, 6.70; N, 11.81.



1: R_1–R_4=H; Fe(Pc)
2: R_2=$COOC_{10}H_{21}$, R_1=R_3=R_4=H; Fe(TDPc)
3: R_2=R_3=$COOC_{10}H_{21}$, R_1=R_4=H; Fe(ODPc)
4: (R_2, R_3)=CON($C_{10}H_{21}$)CO, R_1=R_4=H; Fe(TIPc)
5: R_2=NO_2, R_1=R_3=R_4=H; Fe(TNPc)
6: R_1–R_4=Cl; Fe(Cl_{16}Pc)
7: R_2=R_3=CN, R_1=R_4=H; Fe(OCyPc)

Mössbauer spectra were measured with an Elscint AME-30A spectrometer equipped with a ^{57}Co(Rh) source. The Doppler velocity was calibrated with a metallic ^{57}Fe foil; δ is quoted relative to the centroid of the iron-foil spectrum.

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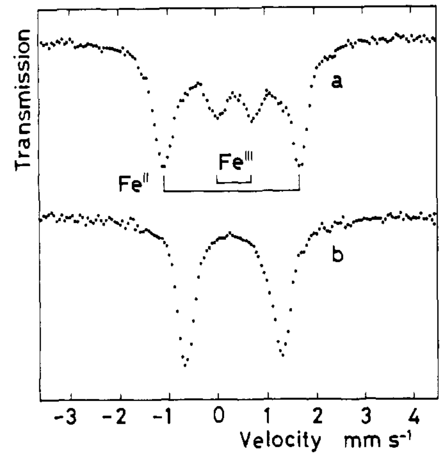

Figure 1. Mössbauer spectra at 4.3 K of (a) Fe(TDPc) and (b) Fe(TIPc).

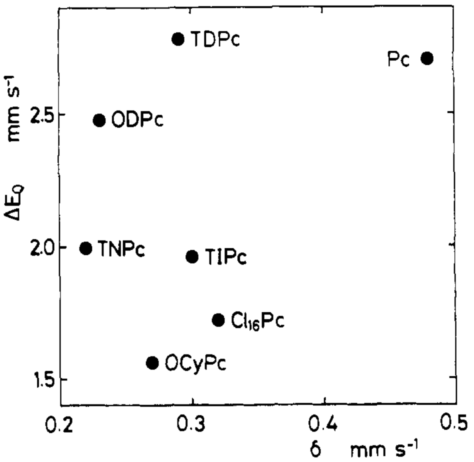

Figure 2. Mössbauer parameters for tetracoordinate (phthalocyaninato)iron(II) complexes at liquid-helium temperature. Phthalocyaninato ligands are indicated.

Results

Mössbauer spectra of polycrystalline solids of the (phthalocyaninato)iron complexes consist of mainly one symmetric quadrupole doublet down to liquid-helium temperatures. The quadrupole splitting values, ΔE_Q's, are nearly temperature-independent, and the isomer shifts, δ's, and ΔE_Q's are in the range typical of $S = 1$ ferrous porphyrins.[23] In some cases, a small component of a quadrupole doublet assigned to ferric high-spin complexes coexists in the spectra. Typical spectra are given in Figure 1. Fe(TDPc) and Fe(ODPc) were shown[21,24] to have ferric high-spin configurations in solutions in chloroform, dichloromethane, benzene, and monochlorobenzene. However, the present work proved that substituted (phthalocyaninato)iron complexes studied have predominantly ferrous intermediate-spin configurations in the solid state, similar to the usual tetracoordinate iron porphyrins and Fe(Pc). In what follows, we shall confine ourselves to $S = 1$ ferrous component of the spectra.

Table I. Mössbauer Data for Tetracoordinate (Phthalocyaninato)- and (Porphyrinato)iron(II) Complexes and Bonding Parameters for Macrocyclic Ligands

	Mössbauer data			bonding parameters		
complex	T, K	δ,[a] mm s^{-1}	ΔE_Q, mm s^{-1}	$\sum\sigma$[b]	Σ	Π
Fe(Pc)[c]	4.2	0.48	2.70	0	10.00	10.48
Fe(TDPc)	4.3	0.29	2.78	1.28	8.99	9.28
	78.8	0.29	2.71			
	298	0.22	2.61			
Fe(ODPc)	4.2	0.23	2.48	2.56	7.02	7.24
	79.3	0.20	2.50			
	298	0.17	2.48			
Fe(TIPc)	4.3	0.30	1.96	2.64	4.97	5.27
	79.3	0.27	1.96			
	298	0.16	1.96			
Fe(TNPc)	4.3	0.22	1.99	2.97	4.52	4.74
	78.5	0.22	1.99			
	298	0.15	2.00			
Fe(Cl$_{16}$Pc)	4.5	0.32	1.72	3.89	3.94	4.27
	78.7	0.32	1.65			
	291	0.25	1.69			
Fe(OCyPc)	4.3	0.27	1.56	4.88	2.69	2.96
	79.0	0.27	1.56			
	298	0.20	1.56			
Fe(OEP)[d]	4.2	0.59	1.60		5.33	5.92
Fe(TPP)[e]	4.2	0.52	1.51		4.35	4.87
Fe(OMTBP)[f]	4.2	0.79	0.63		1.98	2.77

[a] Relative to metallic iron. [b] The sum of the Hammett σ constants for the substituents. References 16, 17, and 26. [c-f] Mössbauer data taken from ref (*c*) 25, (*d*) 28, (*e*) 27, and (*f*) 29.

Mössbauer data are given in Figure 2 and Table I. The latter contains also the sum of the Hammett σ constants[26] for the substituents, $\sum\sigma$, and bonding parameters, Σ and Π, for the ligands that will be discussed later. A random distribution of data points in the δ–ΔE_Q coordinate system is noticed in Figure 2.

Discussion

Mössbauer Parameters. The isomer shift can be written as

$$\delta = \alpha[\rho(0) - \beta] \qquad (1)$$

where $\rho(0)$ is the s-electron charge density in the nuclear volume, α is a constant of negative sign, and β is also a constant depending on the reference material of the shift. Since the core electrons are only slightly influenced by the valence electrons, the principal contribution to the isomer shift comes from changes in the number of electrons in the 4s orbital and from shielding effects owing to electrons in outer 3d and 4p orbitals.

The second Mössbauer parameter ΔE_Q is given by

$$\Delta E_Q = \gamma V_{zz}(1 + \eta^2/3)^{1/2} \qquad (2)$$

where V_{zz} is the principal component of the electric field gradient (EFG) at the nucleus, η is the asymmetry parameter of EFG, and γ is a constant of positive sign. Applied magnetic field Mössbauer measurements on Fe(Pc)[25] and other tetracoordinate planar porphyrin complexes,[27-29] Fe(P), indicate that $V_{zz} > 0$ and $\eta \simeq 0$ in all cases studied. If lattice contributions are ignored, V_{zz} is given approximately[23] by

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(26) Phthalocyanine is an azaporphine to which four benzene rings are fused. The substituent R_2 or R_3 is at the meta position to one exo carbon of a pyrrole ring and at the para position to another exo carbon. Hence, σ_m and σ_p are averaged for R_2 and R_3. R_1 or R_4 is at the ortho and meta positions to the two exo carbons. Although the Hammett relationships fail[15-17] for ortho substituents, $\sigma_m/2$ is adopted for R_1 and R_4. σ values of $COOC_{10}H_{21}$ and $CON(C_{10}H_{21})CO$ are estimated from those of $COOC_2H_5$ and $CONH_2$, respectively.

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$$V_{zz}/e = {}^{4}\!/_{7}\langle r^{-3}\rangle_{\mathrm{d}}\{n(\mathrm{d}_{x^2-y^2}) - n(\mathrm{d}_{z^2}) + n(\mathrm{d}_{xy}) - {}^{1}\!/_{2}[n(\mathrm{d}_{yz}) + n(\mathrm{d}_{zx})]\} + {}^{4}\!/_{5}\langle r^{-3}\rangle_{\mathrm{p}}\{{}^{1}\!/_{2}[n(\mathrm{p}_x) + n(\mathrm{p}_y)] - n(\mathrm{p}_z)\} \quad (3)$$

where $n(\mathrm{d}_i)$ and $n(\mathrm{p}_i)$ are the effective populations of the appropriate 3d and 4p iron orbitals, respectively, and $\langle r^{-3}\rangle$ is the expectation value of $1/r^3$ taken over the appropriate 3d or 4p radial function.

Since both δ and ΔE_Q reflect ligand-to-iron or iron-to-ligand electron donation via a covalent bond, they are expected to correlate with $\sum\sigma$ for the substituents of phthalocyanine. However, the correlation is not clear, as may be seen from Table I and Figure 2. For example, the order of $\sum\sigma$ is Pc < TDPc < ODPc < TIPc; on the other hand, the order of δ is ODPc < TDPc < TIPc < Pc, while that of ΔE_Q is TIPc < ODPc < Pc < TDPc. We therefore examined the Mössbauer data in terms of the differences in the σ- and π-bonding properties of the tetradentate ligands in more detail.

Bonding Parameters. For Fe(Pc) and Fe(P), a number of experimental and theoretical studies are available[25,27-33] that agree on the intermediate spin state ($S = 1$) but differ in their conclusions regarding the ground-state electronic configurations. The two controversial low-lying states are $^3E_g(d_{xy})^2(d_{yz},d_{zx})^3(d_{z^2})^1$ and $^3A_{2g}(d_{xy})^2(d_{yz},d_{zx})^2(d_{z^2})^2$; however, from eq 3 either of the two states leads to a negative V_{zz}, contrary to what is observed.

In their recent work[30] Zerner and co-workers presented an argument in favor of ^3E_g state and succeeded in calculating a positive ΔE_Q of reasonable value for this state. Their success stems from a good deal of covalent mixing between the formally unoccupied $d_{x^2-y^2}$ orbital and the occupied ligand orbitals and from anisotropy in the population of the 4p orbitals. The other configuration $^3A_{2g}$ requires a larger contribution to V_{zz} from covalent electrons to yield a given positive value of ΔE_Q than does the ^3E_g state. The following discussion does not explicitly depend on which configuration the ground state has if the configuration remains the same for the complexes studied.

Two kinds of bonding parameters, Σ and Π, were introduced for a substituted phthalocyanine. They are defined so that Σ is larger for a stronger σ donor, while Π is larger for a stronger π donor and for a weaker π acceptor. Both Σ and Π are relative values: a value of parameter for a particular ligand is not important, but an order of parameter values for different ligands is of significance. The Mössbauer parameters can be related to the bonding parameters by

$$\delta = -\Sigma + \Pi \quad (4)$$

$$\Delta E_Q = a\Sigma - b\Pi + c \quad (5)$$

where a, b, and c are constants and $a > b > 0$.

If a tetradentate ligand is a stronger σ donor, there will be stronger electron donation into formally unoccupied $3d_{x^2-y^2}$, 4s, $4p_x$, and $4p_y$. For $\rho(0)$ in eq 1 the larger 4s occupancy overwhelms other effects: $\rho(0)$ will be larger; hence, δ will be smaller. A larger Σ gives a smaller δ, which corresponds to a negative sign before Σ in eq 4. On the other hand, larger $n(\mathrm{d}_{x^2-y^2})$, $n(\mathrm{p}_x)$, and $n(\mathrm{p}_y)$ in eq 3 lead to a larger ΔE_Q, which corresponds to a positive sign before Σ in eq 5. The constant a gives the ratio of the changes in ΔE_Q and δ.

If a ligand is a stronger π donor and/or weaker π acceptor, the effective populations $n(\mathrm{d}_{yz})$, $n(\mathrm{d}_{zx})$, and $n(\mathrm{p}_z)$ will be larger. The larger shielding effects owing to these electrons make $\rho(0)$ in eq 1 smaller and δ larger. A larger Π gives a larger δ, which corresponds to a positive sign before Π in eq 4. On the contrary, larger $n(\mathrm{d}_{yz})$, $n(\mathrm{d}_{zx})$, and $n(\mathrm{p}_z)$ in eq 3 lead to a smaller ΔE_Q, which corresponds to a negative sign before Π in eq 5. The constant b gives the ratio of the changes in ΔE_Q and δ.

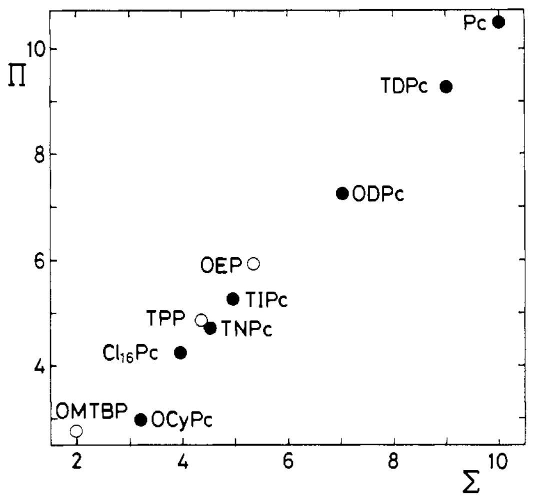

Figure 3. Bonding parameters of substituted phthalocyaninato (closed circles) and porphyrinato (open circles) ligands in tetracoordinate iron(II) complexes.

The condition $a > b$ is derived as follows. By eliminating Π from eq 4 and 5, we get

$$\Delta E_Q = -b\delta + (a - b)\Sigma + c \quad (6)$$

Let us look at the change in ΔE_Q when Σ is varied under the condition of a constant δ; that is, the change in the 4s occupancy is compensated by the change in shielding effects. When Σ increases, the 4s occupancy, $n(\mathrm{d}_{x^2-y^2})$, $n(\mathrm{p}_x)$, and $n(\mathrm{p}_y)$ become larger. Although Π will increase somewhat, the leading contributor to V_{zz} in eq 3 is $n(\mathrm{d}_{x^2-y^2})$; thus, ΔE_Q should increase, which leads to the condition $a > b$. The values of a and b may be determined theoretically, but we took $a = 1.7$ and $b = 1.5$ rather arbitrarily. These values were found to give reasonable results.

The bonding parameters Σ and Π for each ligand were calculated from eq 4 and 5 with δ and ΔE_Q at liquid-helium temperature in Table I. The value of Σ for Pc with no substituent was taken as 10.00, to begin with. Then eq 4 gave Π for Pc as 10.48 and eq 5 gave c as 1.42. With these values of a, b, and c, the parameters Σ's and Π's for other ligands were calculated as shown in Table I and Figure 3.

Bonding Parameters and Hammett Constants. The best known measure of the electron-withdrawing ability of the substituents is the Hammett σ constants. Table I contains the sum of the Hammett σ constants, $\sum\sigma$. The orders of Σ and Π are in a qualitative correlation with $\sum\sigma$: Σ and Π are smaller for a ligand with larger $\sum\sigma$. This relation is explained as follows.

Substituents interact with the macrocyclic ring by both inductive (field) and resonance (conjugation) mechanisms.[16,17,34] The simplest treatment of the inductive effect assumes[34] that a substituent induces a change in the Coulomb integral $\delta\alpha_i$ for only the atom i to which the substituent is bonded. In this case the change in the energy of a molecular orbital j is given by $c_{ji}^2\delta\alpha_i$, where c_{ji} is the MO coefficient. $\delta\alpha_i$ is negative for an electron-withdrawing substituent (positive σ), and its absolute value is larger for a substituent with larger σ. For the phthalocyanines with electron-withdrawing substituents, we expect that every MO shifts to lower energy compared to the corresponding MO for the unsubstituted phthalocyanine, and the energy shift of a given MO should increase with $\sum\sigma$. Several MO's are to be considered. The energy lowering of the σ-donating MO's causes the decrease in the σ donicity to iron $d_{x^2-y^2}$ that lies at higher energy. Thus Σ decreases with $\sum\sigma$. Similarly the energy lowering of the π-donating $e_g(\pi)$ orbitals and π-accepting $e_g(\pi^*)$ orbitals causes the decrease in Π: The π-interacting iron $d_{yz,zx}$ orbitals lie between $e_g(\pi)$ and $e_g(\pi^*)$.

The second mechanism of interaction assumes[34] conjugation of p orbitals of the atoms of the substituents with orbitals of the ring, the conjugation being taken to increase with $\sum\sigma$. The

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σ-donating MO's are not expected to be influenced by the conjugation mechanism. For the substituents with α-carbon or nitrogen, the $e_g(\pi^*)$ level is apparently far from empty or filled 2p orbitals of the substituents, but the filled $e_g(\pi)$ orbitals are relatively close to the filled 2p orbitals. Therefore, the filled $e_g(\pi)$ orbitals are stabilized by conjugation with substituent 2p orbitals that may lie at higher energy than $e_g(\pi)$. For the chlorine substituents, the conjugation of filled 3p orbitals and $e_g(\pi^*)$ should also be taken into consideration. In the case of Pc, the substituents are replaced by hydrogens, which do not permit such conjugation because suitable p orbitals are not available. Thus, the conjugation mechanism is expected to modulate Π in diverse ways depending upon the type of the substituents.

As described above, the inductive mechanism causes the decrease of both Σ and Π with $\sum\sigma$. Equation 4 implies that the difference between Π and Σ is δ. The unsystematic variation of δ with $\sum\sigma$ in Table I is thought to be due in part by the conjugation that modifies only Π diversely. Furthermore, the delicate difference of the effective populations of 3d, 4s, and 4p orbitals must be amplified to give an apparently irregular distribution of data points in Figure 2. We succeeded in extracting information about the σ- and π-bonding properties of the phthalocyaninato ligands from such irregular data.

Porphyrin Complexes. Several tetracoordinate planar porphyrin complexes are included in Table I and Figure 3, for comparison: (octaethylporphyrinato)iron(II), Fe(OEP),[28] (tetraphenylporphinato)iron(II), Fe(TPP),[27] and (octamethyltetrabenzoporphyrinato)iron(II), Fe(OMTBP).[29] The basicity is thought to decrease in the order Pc > OEP > TPP > OMTBP, on the basis of redox potentials of the porphyrins and other experimental results. The calculated values of bonding parameters also decrease in the same order: decreasing the porphyrin basicity places less electron density on the iron. Reasonable orders of bonding parameters were obtained on the basis of the assumption that the ground-state configurations in these complexes are the same as in the (phthalocyaninato)iron(II) complexes. Although some studies suggest[30,33] a ground state for (porphyrinato)iron(II) different from that for (phthalocyaninato)iron(II), the present study favors the same configuration in these two systems.

The values of a and b in eq 5 are rather ambiguous, as stated above. Detailed considerations proved, however, that b should be larger than 0.421 in order to give a larger Σ for Pc than for other substituted phthalocyanines, a should be smaller than 1.775 in order to give a smaller Π for OMTBP than for all phthalocyanines, and any pair of a and b satisfying $0.421 < b < a < 1.775$ does not change the orders of Σ's and Π's in Table I and Figure 3. Our determination of the bonding parameters is believed to be adequate.

Conclusion

Two kinds of bonding parameters, Σ and Π, were introduced for substituted phthalocyanines to interpret Mössbauer parameters, δ and ΔE_Q, of tetracoordinate (phthalocyaninato)iron(II) complexes in connection with the bonding characteristics of the macrocyclic ligands. They represent σ- and π-bonding properties, respectively, and are defined to be larger when more electron density is placed on the iron. The orders of calculated Σ and Π are in a good correlation with the sum of the Hemmett σ constants, $\sum\sigma$, of the substituents.

Several tetracoordinate (porphyrinato)iron(II) complexes were treated in the same manner. The bonding parameters, Σ and Π, are found to decrease in the decreasing order of the basicity of the porphyrinato ligands. The present study favors the same ground-state configuration for (porphyrinato)iron(II) as for (phthalocyaninato)iron(II).

In sum, the apparently irregular variation of δ and ΔE_Q of tetracoordinate iron(II) complexes is interpreted systematically. A study of (phthalocyaninato)iron(II) complexes with electron-releasing substituents is in progress.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, No. 61540456.

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Time-Resolved FTIR Study of the Adsorption and Reaction of $Co(CO)_3NO$ on Alumina

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Received October 27, 1986

Deposition of $Co(CO)_3(NO)$ gas on alumina preactivated at 450 °C occurs readily at room temperature to yield two mononitrosyl species with $\nu(NO)$ at 1795 and 1700 cm^{-1}, respectively. Time-resolved FTIR spectroscopy shows that within minutes these initial species start to react and yield more than one type of surface isocyanate, $(NCO)_s$, as well as other surface nitrosyl species. Without evacuation of the reactant, $(NCO)_s$ formation proceeds slowly over a 7-day period, accompanied by the appearance of bands due to a surface dinitrosyl with $\nu(NO)$ at 1880 and 1800 cm^{-1}, and CO is released to the gas phase. The formation of $(NCO)_s$ is greatly accelerated under vacuum, but the predominant surface nitrosyl generated is now a mononitrosyl with $\nu(NO)$ at 1830 cm^{-1}. The latter is easily converted into the 1880/1800-cm^{-1} dinitrosyl species in the presence of CO. Codeposition of $Co(CO)_3(NO)$ with an excess of either CO or NO very efficiently inhibits the formation of isocyanates. In the presence of CO, the 1795- and 1700-cm^{-1} species show no sign of significant decomposition even after 4 days. Under NO, however, they are converted into the 1880/1800-cm^{-1} dinitrosyl species.

Introduction

NO gas has frequently been used as a chemical probe to assess the nature of metallic sites present on a surface following deposition of a suitable metallic precursor (see for example ref 1). An alternative and complementary approach is to deposit a metallic element with the NO probe already attached to it. For example, $Mo(CH_3CN)_4(NO)_2^+BF_4^-$ deposited on alumina has provided a model for NO reactions on Mo/Al_2O_3 surfaces.[2]

Although there have been many studies of the deposition of metal carbonyls on various surfaces,[3] including $Co_2(CO)_8$ on alumina (see ref 4 and 5 and references therein), the use of

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