reaction. Work along these lines is now in progress.

Acknowledgment. Calculations have been carried out at the Centre de Calcul du CNRS in Strasbourg-Cronenbourg. We thank the staff of the Centre for their cooperation. Some initial calculations on this reaction were done in our group by Dr. A. Rossi. This work has been supported through ATP No. 3790 of the CNRS.

Registry No. 3a, L = PH_3, 72152-08-0; **4a**, L = PH_3, 72152-09-1; **4b**, L = PH_3, 72173-82-1; **4c**, L = PH_3, 72173-87-6; $RhCl(PPh_3)_3$, 14694-95-2.

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Iron–Oxygen Interactions in an Argon Matrix

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Received July 8, 1980

The interaction of iron atoms with oxygen molecules and atoms in an argon matrix over the temperature range from 15 to 40 K has been examined. The iron atoms are produced by a hollow-cathode sputtering device. Iron–oxygen complexes are identified by oxygen-18 isotope shifts in the infrared spectra, annealing behavior, and comparison to known compounds. A band at 956 cm^{-1} is assigned to the O–O stretching frequency of a side-bonded FeO_2 structure, an assignment at variance with current literature. A band at 872 cm^{-1} is assigned to FeO while a band at 969 cm^{-1} is assigned to an Fe–O stretching mode of linear O–Fe–O. A band at 946 cm^{-1} is tentatively assigned to metastable bent O–Fe–O species which disappears upon annealing the matrix at 25 K. Oxygen atoms are formed on the surface of the matrix during its formation by the reaction of O_2 molecules with excited argon atoms from the hollow-cathode discharge. The verification of the existence of a stable FeO_2 complex which still contains an O–O bond lends credence to the proposal of a molecularly adsorbed O_2 precursor state in iron oxidation.

Introduction

The interaction of oxygen with Fe atoms is of interest because of its bearing on such diverse processes as corrosion of structural metals and oxygen transport in biological systems. There have been a number of reports on the kinetics and the surface-phase structure produced in the early stages of the interaction between a pure iron surface and oxygen.[2-10] Recent detailed examination of the kinetics of the O_2 interaction have lead to the suggestion of molecularly adsorbed O_2 as a precursor state to dissociation into immobile adsorbed oxygen atoms.[9,10] The nature of the adsorbed O_2 precursor state or the nature of the sites required to dissociate O_2, if indeed there are any requirements for O_2 dissociation, have not been discussed. In this paper the results of using matrix isolation spectroscopy to examine the initial interaction between Fe atoms and oxygen are reported and the implications with respect to oxygen adsorption on metallic iron discussed.

The interaction of oxygen with Fe atoms coordinated in biological systems has been the subject of several studies.[11-15] Infrared and Raman spectra have been interpreted[13,15] as indicating the O_2 is end bonded, as opposed to side bonded, to Fe atoms in 2+ or 3+ oxidation states. A generalized valence-bond calculation was found to favor end bonding over side bonding in an $Fe^{II}O_2$ modeling of the biological system.[16]

In contrast to these iron biological systems, a general review[17] of dioxygen in inorganic coordination complexes reveals an overwhelming preference for a side-bonded structure. For isolated iron atoms in an argon matrix one study[18] has suggested a side-bonded interaction for O_2. The reasons for Fe atoms behaving differently from Fe in iron(II) porphyrin and hemerythrin are not clear. This difference suggested to us that a more thorough study of the Fe matrix system was desirable.

The ground-state properties of molecular FeO also has been the subject of some disagreement. The Fe–O stretching frequency has been reported[18] to be at 872 ± 1 cm^{-1}. However a recent paper[19] claims it to be at 943 cm^{-1}. The value now appers to have been definitely settled[20] to be 880 cm^{-1}, and our work reported here is in agreement with this value.

Experimental Section

The cryostat used was a Cryogenic Technology Inc. Spectrim TM helium cryogenic cooler. The cold window and external windows of the vacuum system along the optical path were all potassium bromide. The temperature of the cold window was measured with use of a gold (0.07% Fe) vs. chromel thermocouple soldered on the copper window support with indium solder.

Iron atoms were produced by an electric discharge in the argon system with use of an iron foil as the cathode. The device used in

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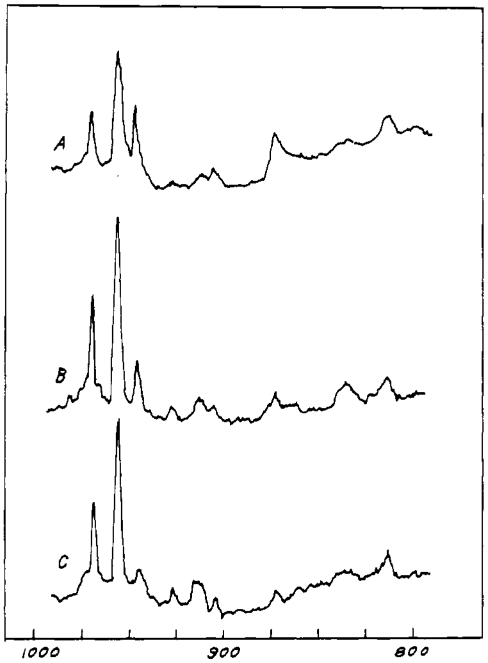

Figure 1. Infrared spectrum (cm^{-1}) of Fe atom–oxygen interaction using an O_2/Ar ratio of 1/60: A, unannealed; B, annealed for 10 min at 25 K; C, annealed for 10 min at 30 K.

this study was a modification of the hollow-cathode sputtering device developed by Carstens, Kozlowski, and Gruen.[21] The iron used in this study was 99.99% pure iron foil supplied by the Alfa Division of Ventron, Danvers, MA. Matheson's ultra-high-purity argon and Airco's high-purity oxygen were used without further purification. For isotope studies, $^{18}O_2$ of purity 90–99% from the Mound Facility, Monsanto Research Corp., Miamisburg, Ohio, was used. A Perkin-Elmer 457 infrared spectrometer and a Cary 14 spectrometer for visible and ultraviolet spectra were used. Complete details of the experimental equipment are given in ref 22.

An oxygen–argon gas mixture was introduced into the sample chamber through a separate inlet from the Fe atom bearing gas for cocondensation on the KBr sample window. The condensing temperature of matrix gas was always in the range of 14–16 K. Argon and oxygen gas flows were regulated with use of needle valves. The mole ratios of oxygen to argon were $^{16}O_2/Ar = 1/60$, 1/120, and 1/240. The concentrations of iron atoms in the matrix were adjusted by changing the current intensities and the flow rate of the matrix gas. Though the exact atomic and diatomic concentration of iron in the matrix were not measured, the qualitative abundances could be observed with use of ultraviolet and visible spectra of the matrices.[23,24]

Results

The infrared spectra in the 1000–800-cm^{-1} range of the species formed in the Ar matrix by using a 17 mmol/h flow with a 50 mA current to produce a matrix with an O_2/Ar ratio of 1/60 (our highest O_2 concentration) is shown in Figure 1. The spectra show four main features at 969, 956, 946, and 872 cm^{-1}. The most stable band at 956 cm^{-1} grows with annealing to 30 K. The total annealing regime consists of heating the sample to 20, 25, 30, 35, and 40 K for 10 min at each temperature with the sample being returned to 15 K after 10 min at each temperature to record an infrared spectrum. The band at 946 cm^{-1} decreases rapidly with annealing while the 969-cm^{-1} band first grows and then decreases a little. At 40 K all bands decrease rapidly.

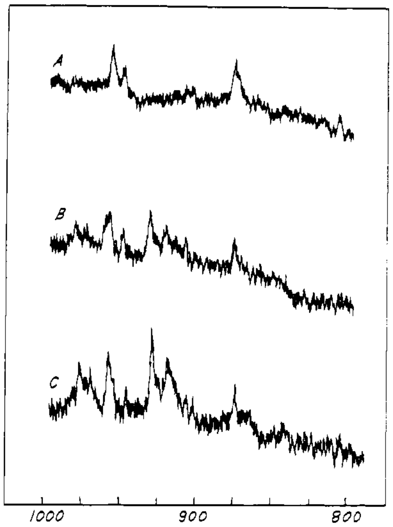

Figure 2. Infrared spectrum (cm^{-1}) of Fe atom–oxygen interaction using an O_2/Ar ratio of 1/240: A, unannealed; B, annealed for 10 min at 25 K. C.; C, annealed for 10 min at 30 K.

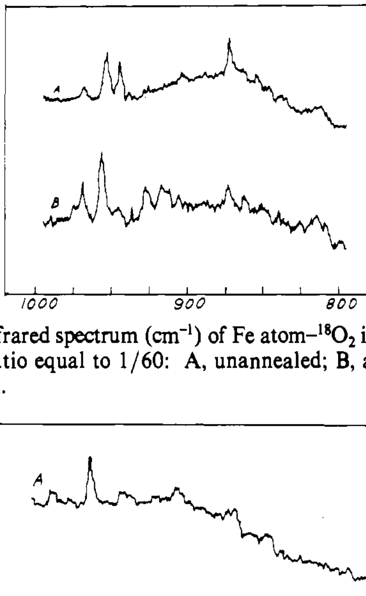

Figure 3. Infrared spectrum (cm^{-1}) of Fe atom–$^{18}O_2$ interaction using an O_2/Ar ratio equal to 1/60: A, unannealed; B, annealed for 10 min at 30 K.

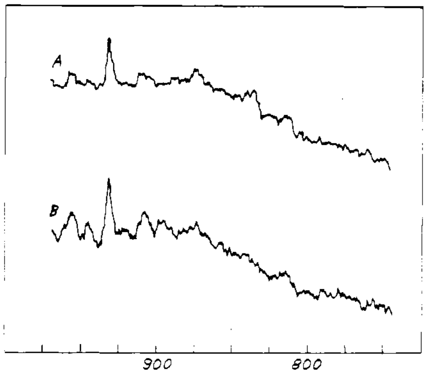

Figure 4. Infrared spectrum (cm^{-1}) of Fe atom interaction with 25% $^{16}O_2$, 50% ^{16}O–^{18}O, and 25% $^{18}O_2$ gas using an O_2/Ar ratio equal to 1/60: A, unannealed; B, annealed for 10 min at 25 K.

The result of lowering the O_2/Ar ratio to 1/240 is shown in Figure 2. All other variables are kept the same as those for Figure 1. As a consequence of the lower O_2 concentration, the species producing the 969-cm^{-1} band is absent in the unannealed sample, but it does form upon warming of the matrix. The intensity of the 956-cm^{-1} band is reduced by the lowered O_2 concentration. The decreased O_2 concentration increases the Fe/O_2 ratio with the result that the bands in the 900–940-cm^{-1} region, which are relatively minor in Figure 1, become the most prominent bands in Figure 2 after annealing to 30 K.

Experiments with $^{18}O_2$ were performed so that isotope shifts would be available in assigning bands to structures. In order to conserve $^{18}O_2$, we used a small reservoir bulb. Using the

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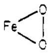
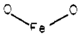
Table I

band, cm^{-1}			assignt		$\Delta\nu/\nu$	
$^{16}O_2$	$^{18}O_2$	$^{16}O^{18}O$			calcd	exptl
969	932		O–Fe–O	Fe–O str Fe–O bend	0.036 0.037	0.038
956	906	931		O–O str Fe–O_2 str	0.051 0.036	0.052
946 517^a	911 494^a			Fe–O str Fe–O bend	0.039 0.044	0.037 0.044
872			Fe–O		0.044	0.044

[a] From ref 18a.

same conditions as in Figure 1 but with $^{18}O_2$ produced the spectra in Figure 3. In Figure 4 the result of using an oxygen mixture containing 25% $^{16}O_2$, 50% ^{16}O–^{18}O, and 25% $^{18}O_2$ is shown. The isotopically shifted bands are correlated with $^{16}O_2$ bands on the basis of relative intensities and behavior upon annealing. The band correlations, values for $\Delta\bar{\nu}/\bar{\nu}_{16}$ where $\Delta\bar{\nu} = \bar{\nu}_{16} - \bar{\nu}_{18}$, and structural assignments are given in Table I. The most intense band in the $^{18}O_2$ spectra in Figure 3 at 906 cm^{-1} is correlated with the most intense band at 956 cm^{-1} in the $^{16}O_2$ spectra in Figure 1. The annealing behavior of these two bands is also the same. This correlation, which appears quite unequivocal on the basis of Figures 1 and 3, is important because it establishes a band assignment at variance with a previously published one.[18a] The 932-cm^{-1} band in Figure 3 grows in intensity with annealing to become the second most intense band in the annealed spectrum, so it is correlated with the 969-cm^{-1} band in Figure 1 which behaves in the same manner. Likewise the band at 911 cm^{-1} in Figure 3 correlates with the 946-cm^{-1} band in Figure 1, which also decreases upon annealing.

The main feature of interest in Figure 4 is the single intense band at 931 cm^{-1}. This band is assigned to an ^{16}O–^{18}O containing species because it correlates with the 956-cm^{-1} band for an $^{16}O_2$ species in Figure 1 and the 906-cm^{-1} band for an $^{18}O_2$ species in Figure 3. The occurrence of a single intense band suggests a symmetric structure, which we assign as O_2 side bonded to Fe, rather than end-bonded O_2 which should give two bands of equal intensity for ^{16}O–^{18}O.

The presence of iron atoms in the matrix was verified by comparing the UV and visible spectrum of Figure 5 with published spectra[23,24] for Fe atoms. The spectrum in Figure 5 is a record of the unannealed sample used to obtain the IR data in Figure 3. The presence of Fe_2 dimers is indicated by the broad bands at 4500 and 5400 Å as published.[24] Similar spectra were obtained for the sample used in Figure 4. The visible spectrum for the high O_2 concentration sample of Figure 1 showed no evidence of the presence of Fe_2 while the visible spectrum for the low O_2 concentration sample of Figure 2 shows a larger amount of Fe_2 than that present in the sample of Figure 3.

Also present in the IR spectra were bands at 1310, 1301, 1118, and 1039 cm^{-1}. These bands are also present when Cu is sputtered and show isotope shifts when $^{18}O_2$ is used indicative of oxygen stretching bands. Comparison to known spectra[25] indicate that the 1118-cm^{-1} band is due to O_2^-, perhaps loosely associated with another species in the matrix, and the 1039-cm^{-1} band to ozone. The 1118-cm^{-1} band disappears rapidly with annealing as would be expected for a charged species once the matrix is warmed enough to permit some mobility of species. The 1039-cm^{-1} band is quite stable until extensive annealing at 35–40 K occurs. The spectra using $^{18}O_2$ contain a band at 938 cm^{-1} which is in good agreement with the reported[26] matrix spectrum for $^{18}O_3$. No evidence for interaction between ozone and iron was found before the disappearance of O_3 at 35–40 K which is presumed to be due to its interaction with clusters of Fe atoms.

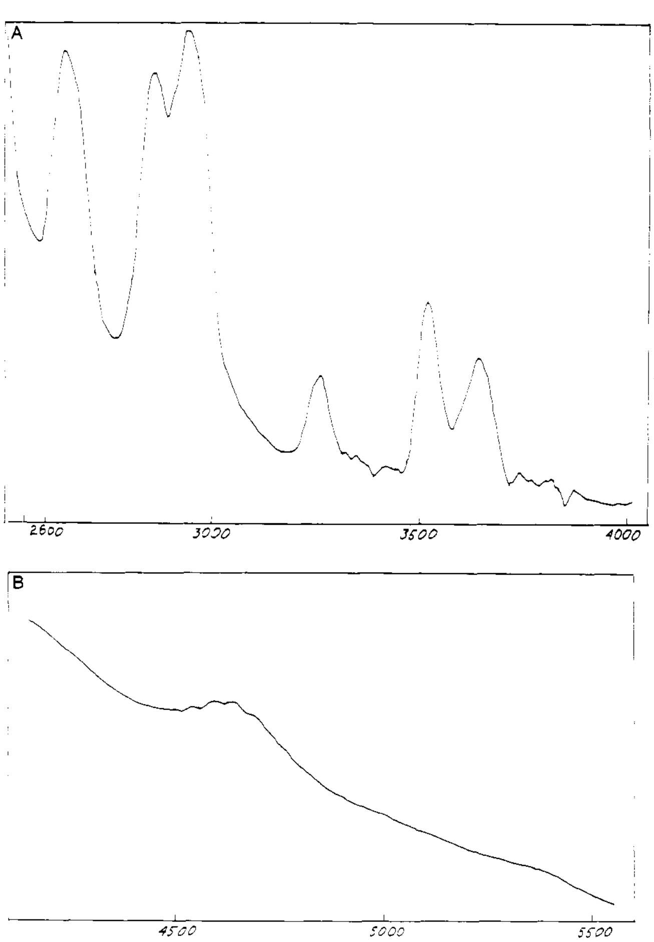


Figure 5. (A) UV spectrum (Å) and (B) visible spectrum (Å) of the unannealed sample from Figure 3.

Discussion

The observed spectra may be accounted for by assuming that the initial species arriving at the matrix surface are individual Fe atoms, O_2 molecules, and Ar*, where the asterisk indicates an electronically excited atom. The Fe_2 species are presumed to be formed at the matrix surface as indicated by the work of Moscovits and Ozin.[27] That Fe_2 is not formed in the hollow-cathode sputtering process is indicated by the observation that at high O_2 concentrations Fe_2 is not found since formation of Fe_2 during sputtering would not be affected by O_2 concentration in the O_2 gas stream. In contrast Fe_2 formation at the matrix surface would be decreased by a high O_2 concentration reacting rapidly with Fe atoms.

While not directly observed, the presence of O atoms is indicated by the presence of O_3 which is probably formed by the reaction of O_2 with O atoms in the presence of matrix atoms which remove the excess energy. The interaction of Ar* from the sputtering plasma with O_2 molecules would account for the presence of O atoms and O_2^- ions.

The band at 872 cm^{-1} is assigned to the diatomic molecule FeO on the basis of agreement with previous assignments[18,20] for this band and the isotope shift agreeing with the value calculated for FeO. The only question about this assignment is that one paper[19] has recently assigned the ground-state vibration of FeO at 943 cm^{-1}. However it seems unlikely that

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(25) L. Andrews, <<latCryochemistry", Edited by M. Moskovits and G. A. Ozin, Eds., Wiley, New York, 1976, Chapter 6.

(26) L. Andrews and R. C. Spiker, Jr., *J. Phys. Chem.*, **76**, 3208 (1972).

(27) M. Moskovits and G. A. Ozin, "Cryochemistry", Wiley, New York, 1976, Chapter 9.

the matrix species observed here and by others[18,20] is not the ground-state species. The FeO molecules in our matrix are probably formed by the interaction of Fe atoms with O atoms at the matrix surface. This is supported by the observation that a band at 872 cm^{-1} is not observed when Fe atoms are evaporated into a O_2–Ar matrix from a Knudsen cell.[18a] FeO has previously been formed in a matrix by cocondensing Fe atoms and N_2O molecules.[18a]

The infrared bands at 969, 956, 946, and 872 cm^{-1} are all assigned to species containing one Fe atom for the following reasons.

(1) The UV and visible spectrum in Figure 5 shows that the overwhelming metal species in the matrix are isolated iron atoms. Therefore oxygen species are far more likely to contact Fe atoms than Fe polymers, so that the most prominant complexes should contain one Fe atom.

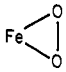
(2) The presence of FeO, confirmed by comparison to known spectra and its isotope shift, shows that single Fe atom species exist in the matrix. If Fe atoms had the mobility to react with all other single Fe atom complexes, they would have also reacted with all FeO so it would not be present.

(3) Other workers have done a large amount of work which indicated that, under similar conditions to ours, the predominant species contain one metal atom.[27]

(4) Using a lowered amount of O_2 shows in Figure 2 that the 900–940-cm^{-1} bands grow relative to the 969, 956, and 946 cm^{-1} bands so that 900–940-cm^{-1} bands are probably multiple Fe species, leaving the others by their contrasting behavior to be single Fe atom complexes.

(5) When a 20-mA current rather than the usual 50-mA current was used in the sputtering, the 969-, 956-, 946-, and 872-cm^{-1} bands dominate the spectra as usual and the 900–940-cm^{-1} absorptions are greatly reduced.

The band at 956 cm^{-1} is assigned to an FeO_2 structure on the basis of its stability and the isotope shift agreeing with that calculated for the O–O stretch of O_2 loosely bound to a metal atom. The observation of three bands at 956, 931, and 906 cm^{-1} in an approximate intensity ratio of 1/2/1 in Figure 4 when 25% $^{16}O_2$, 50% ^{16}O–^{18}O, and 25% $^{18}O_2$ are used strongly suggests the symmetric side-bonded structure



If an end-bonded Fe–O–O structure were formed, a set of four equal-intensity lines would be expected in the mixed-isotope experiment. It has been noted that, if the M–X bond in end bonded M–X–X is weak, the central two lines could be close enough together to appear as a single band.[28] For an examination of this possibility calculations for Fe–O–O were made for ^{16}O–^{18}O bonded on either end with use of various force constants for the Fe–O bond. If the Fe–O force constant is high enough that the Fe–O stretching frequency is above 400 cm^{-1}, then the separation of the two central bands in the quartet for the mixed isotopes would be over 20 cm^{-1}, a readily observable difference. When the Fe–O stretching frequency is below 300 cm^{-1}, the separation is 7 cm^{-1} or less, which becomes more difficult to distinguish. Unfortunately no Fe–O stretch could be definitely observed. In metalloproteins, the Fe–O stretching frequency has been observed[29,30] at 568 cm^{-1}. This suggests that for O_2 end bonded to Fe the separation of the two center bands of the quartet for the mixed isotopes should be readily observable. Since only three bands were observed, the side-bonded form is indicated. A further argument against the end-bonded species occurring but not having the separation of the two central bands of the mixed isotopes observable is that $\Delta\nu/\nu$, where $\Delta\nu$ is $\nu(^{16}O{-}^{16}O) - \nu(^{18}O{-}^{18}O)$, is calculated to be 0.058 when the Fe–O force constant is low whereas $\Delta\nu/\nu$ is calculated to be 0.0546 when the force constant is large enough to produce four readily observable bands in the mixed-isotope experiment. The experimental value is seen in Table I to be 0.052, indicating that the Fe–O force constant is realtively large.

The bands at 969 and 946 cm^{-1} have values of $\Delta\nu/\nu$ of 0.038 and 0.037, respectively, which strongly suggests that these bands are due to O–Fe–O stretching bands. The 946-cm^{-1} band readily disappears upon matrix annealing as is characteristic of metastable species. No direct experimental evidence for the O–Fe–O angle is available, but MINDO calculations done in our laboratory give a linear O–Fe–O structure lowest in energy and a metastable bent O–Fe–O structure. Therefore the O–Fe–O structure giving the 969-cm^{-1} band is tentatively assigned a linear structures and the 946-cm^{-1} band to a bent O–Fe–O configuration.

On the assumption that the intensity of the band at 956 cm^{-1} for FeO_2 is directly proportional to the O_2 concentration in the matrix, the rate for formation of linear O–Fe–O, as indicated by the intensity of the 969-cm^{-1} band, is more than first order in oxygen. This follows from the strong dependence of the 946-cm^{-1} band on the oxygen concentration shown in Figures 1 and 2. This suggests a mechanism of formation of

$$2O + Fe \rightarrow O{-}Fe{-}O \qquad (1)$$

where the oxygen atom concentration in the matrix is determined by the rate of the process

$$Ar^* + O_2 \rightarrow 2O + Ar \qquad (2)$$

which would be first order in O_2 concentration. For eq 1 to be second order in oxygen atom concentration it must be assumed that the two oxygen atoms were formed independently. Thus the linear O–Fe–O is *not* formed by the process

$$Ar^* + FeO_2 \rightarrow O{-}Fe{-}O + Ar \qquad (3)$$

The intensity of the 946-cm^{-1} band assigned to metastable bent O–Fe–O (designated O–Fe–O(m)) is proportional to the intensity of the 956-cm^{-1} band for FeO_2 in the unannealed spectra. This suggests that it is formed from a single O_2 molecule which could be by either eq 4 or 5.

$$FeO_2 + Ar^* \rightarrow O{-}Fe{-}O(m) + Ar \qquad (4)$$

$$Fe + O_2 \rightarrow O{-}Fe{-}O(m) \qquad (5)$$

Because the bands in the 900–940-cm^{-1} region develop most prominently when the O_2/Fe ratio is low, these bands are presumed to be due to Fe_xO_y species where $x \geq 2$. We are not at present prepared to discuss these bands in detail.

The data and interpretation presented here are consistent with the data presented in ref 18a, but the band assignments differ in some respects. The band assignments in ref 18a are reasonable on the basis of the data therein, but the additional data we obtained, particularly the annealing data, together with the isotope shift calculations dictate the new assignment herein. Both in our work and that of ref 18a the ^{16}O species band at 946 cm^{-1} shifts to 911 cm^{-1} for ^{18}O and diminishes rapidly upon annealing. The isotope shift of 0.037 for $\Delta\nu/\nu$ found in both works is not possible for an O–O stretch in side-bonded FeO_2 as assigned in ref 18a but is compatible with an O–Fe–O molecule, either bent or linear. In ref 18a a band at 517 cm^{-1} with an isotope shift of 0.044 for $\Delta\nu/\nu$ was found and associated with the species producing the 946-cm^{-1} band. The 517-cm^{-1} band is assigned in ref 18a to the Fe–O stretch in side-bonded FeO_2, but their observed isotope shift is not compatible with this assignment because the isotope shift

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(28) J. K. Burdett, A. J. Downs, G. Gaskill, M. A. Graham, J. J. Turner, and R. F. Turner, *Inorg. Chem.*, **17**, 523 (1978).

(29) H. Brunner, *Naturwissenschaften* **61**, 129 (1974).

(30) J. M. Burke, J. R. Kincaid, S. Peters, R. R. Gagyne, J. P. Collman, and T. G. Spiro, *J. Am. Chem. Soc.*, **100**, 6083 (1978).

should be 0.036 for this vibration. An isotope shift of 0.044 is calculated for the bending vibration in O–Fe–O with a 120° bond angle. Thus the isotope shift for the 517-cm^{-1} band is compatible with our assignment of 946 cm^{-1} to bent O–Fe–O. The isotope shift for a linear O–Fe–O molecule should be 0.037 which rules out a linear O–Fe–O structure for the molecule giving the 946-cm^{-1} band and leaves as still reasonable our assignment of the 969-cm^{-1} band to linear O–Fe–O.

Some spectral features which we observe were not observed in ref 18a apparently because their spectra are much less intense than ours. In ref 18a it is noted that with annealing the 956- and 969-cm^{-1} bands increase relative to the 946-cm^{-1} band which decreases with annealing but, their spectra were too weak to get isotope shifts for these more stable species as we did. Some differences in relative intensity among these bands between the two works are probably due to the different methods of producing Fe atoms. In ref 18a the Fe atoms are produced by evaporation at 1950 K which suggests the O–Fe–O linear and metastable bent molecules are formed by energetic Fe atoms colliding with O_2 molecules at the matrix surface. In this work the Fe atoms are sputtered into Ar gas not over several hundred degrees (°C). Under these conditions with Ar* and O atoms present the O–Fe–O species are believed formed by the mechanisms given previously.

The verification of the existence of a stable FeO_2 complex which still contains an O–O bond lends credence to the proposal of a molecularly adsorbed O_2 precursor state in iron oxidation. Although previously reported[18a] the present results indicate that the infrared band previously assigned to FeO_2 is for a species that does not contain an O–O bond. The stability of the FeO_2 complex in the 15–25 K range indicates that in the interaction of O_2 with a single Fe atom there is at least a small activation energy for the dissociation of the O–O bond. The disappearance of the band for the O–O stretch at 35–40 K could be FeO_2 acquiring sufficient energy to break the O–O bond or to Fe cluster formation furnishing multiple Fe sites upon which O–O bond rupture occurs with very little or no activation energy. In the many annealing experiments performed no tendency for the 969-cm^{-1} band to grow at the expense of the 956-cm^{-1} band was observed as would be the case if O–O bond breaking were occurring in FeO_2. Also experiments were performed in which a 20-mA current was used in the hollow-cathode discharge rather than the usual 50 mA current so that the Fe atom concentration was considerably reduced. In these runs the 956-cm^{-1} band for FeO_2 was not reduced in intensity after 10 min at 40 K. This indicates that O–O bond rupture occurs more readily on iron sites involving several iron atoms than on single Fe atoms.

Acknowledgment. We thank the National Science Foundation and Seoul National University, Seoul, Korea, for support of this work.

Registry No. O–Fe–O, 12411-15-3; FeO_2, 58220-66-9; FeO, 1345-25-1; ^{18}O, 14797-71-8.

Contribution from the Department of Chemistry,
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Matrix-Isolation Studies of Lewis Acid/Base Interactions: Infrared Spectra of the 1:1 Adduct $SiF_4{\cdot}NH_3$

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Received February 19, 1981

The codeposition of NH_3 and SiF_4 into inert matrices at dilutions as high as 1/1/4000 gives rise to an extremely sharp set of product bands, at 409, 456, 706, 854, 952, and 1253 cm^{-1}. Consideration of the isotopic shifts of these bands and comparison to spectra of the known 1:2 adduct indicate that these bands can be assigned to a 1:1 adduct, $SiF_4{\cdot}NH_3$. The spectra also suggest a trigonal-bipyramidal arrangement about the central silicon, with the NH_3 group in an axial position. The codeposition of $SiCl_4$ with NH_3 gave rise to product bands as well, but only when relatively high concentrations were employed. These bands are ascribed to a 1:1 adduct as well, which is considerably less strongly bound than the SiF_4 analogue. The matrix codeposition of SiF_4 with dimethyl ether did not give rise to any product bands, indicating that a stable adduct is not formed.

Introduction

Complexes between strong Lewis acids and bases have been known for a number of years,[1-3] especially for such Lewis acids as BF_3 and PF_5. Similar complexes for relatively strong Lewis acids such as SiF_4 are not as well characterized, although a number have been discovered. With very strong bases such as trimethylamine, SiF_4 forms 1:1 and 1:2 complexes, both of which can be isolated at room temperature.[4-6] For the strongest base known (using a gas-phase proton affinity scale), the fluoride anion F^-, both 1:1 adducts (SiF_5^-)[7] and 1:2 adducts (SiF_6^{2-})[8] are known as well. However, with somewhat weaker bases such as NH_3, hydrazine,[9] or dimethylformamide[10] only 1:2 adducts have been observed. The complex $SiF_4{\cdot}2NH_3$ has been isolated in the solid phase, where it is the oldest known compound containing a Si–N bond;[11] in the gas phase, virial coefficients and dissociation data for the reaction $SiF_4{\cdot}2NH_3(s) \rightleftarrows SiF_4(g) + 2NH_3(g)$ have been obtained.[12,13]

At the same time, studies of the Lewis acid/base chemistry of the silicon tetrahalides from SiF_4 to SiI_4 demonstrate a large difference in reactivity. Several studies have shown that $SiCl_4$ will react with a number of bases to form distinct products,[14,15] while SiF_4 forms adducts with these bases. At the same time, workers have shown that the order of stability of the silicon tetrahalides toward a standard base depends on the base chosen (hard vs. soft), and these results show that $SiCl_4$ and $SiBr_4$ are softer acids than SiF_4, as might be anticipated.[16] Also,

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