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Reversible Adsorption of Oxygen on Silica Gel Modified by Imidazole-Attached Iron Tetraphenylporphyrin

Orlando Leal, David L. Anderson, Robert G. Bowman,
Fred Basolo,* and Robert L. Burwell, Jr.*

Contribution from the Department of Chemistry and the Ipatieff Laboratory,
Northwestern University, Evanston, Illinois 60201. *Received December 16, 1974*

Abstract: Oxygen adsorbs reversibly on an iron(II) porphyrin attached to the imidazole groups of a silica gel containing 3-imidazolylpropyl groups bonded to surface atoms of silicon. The chemisorption of oxygen is weak at 0°, rather strong at −78°, and irreversible at −127°. Each iron atom can adsorb one molecule of oxygen, a result in accord with formation of a monoadduct of the type $Fe-O_2$. Similarly, carbon monoxide is reversibly adsorbed by the activated modified gel giving the adduct Fe-CO. Worthy of note is the fact that the adsorbent is stable in oxygen at room temperature, presumably because the attachment of iron porphyrin to the rigid support prevents the dimerization to form $Fe^{III}-O-Fe^{III}$ which usually takes place.

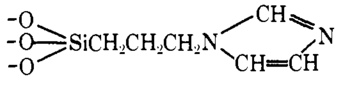
One of the major difficulties encountered in attempts to prepare monomeric iron-oxygen adducts, particularly adducts of iron porphyrins, is preventing the conversion of the adduct to the μ-oxo dimer

$$Fe(II) + O_2 \rightleftharpoons Fe\text{-}O_2 \xrightarrow{Fe(II)} Fe^{III}\text{-}O\text{-}Fe^{III}$$

Considerable recent work has been aimed at overcoming this problem, and two approaches have been successful. In the first, the reactions are carried out at a temperature so low that the reactions leading to dimerization are very slow but high enough so that the formation of adduct proceeds readily.[1,2] Such a temperature is about −78°. In the second, porphyrins have been substituted in a fashion that inhibits dimerization. By this means reversible reaction between oxygen and Fe(II) porphyrins in solution has been achieved at room temperature.[3,4]

An additional approach would be to attach the iron complex to the surface of a solid so that two iron atoms could not approach each other in such a manner as to lead to dimerization. Wang[5] reported spectral evidence that oxygen binds reversibly to 1-(2-phenylethyl)imidazoleheme diethyl ester embedded in a matrix of an amorphous mixture of polystyrene and 1-(2-phenylethyl)imidazole. However, Collman and Reed[6] reported that cross-linked polystyrene containing imidazole ligands was a support not rigid enough to prevent dimerization and that, upon treatment with oxygen, μ-oxo dimer was extracted by benzene from tetraphenylporphyriniron(II) attached to the modified polystyrene.

Attachment of an iron porphyrin to a rigid support should better inhibit dimerization. We had prepared a number of modified silica gels for use as selective adsorbents and catalysts.[7,8] One of these[7] contained surface 3-imidazolylpropyl groups



to which it should be possible to attach iron(II) porphyrins. This has been done and it has led to the preparation of an adsorbent to which oxygen binds reversibly and which is stable in oxygen even at room temperatures.

Experimental Section

Surface Modification. The imidazolylpropyl gel was prepared as previously described.[7] Ten grams of 60-80 mesh Davison grade 59 silica gel (a wide-pore gel with a nominal pore diameter of 14 nm, a specific area of 340 m^2, and a pore volume of 1.1 cm^3/g) was dried in the oven at 150° and refluxed in *m*-xylene with 2 g of imidazole and 3 g of redistilled 3-chloropropyltrimethoxysilane. Different coverages were obtained by varying the time of reflux from 45 min to 9 hr. The product was washed consecutively in the absence of moisture with benzene and acetone to produce a modified imidazolyl hydrochloride gel. The gel was dehydrochlorinated by treatment with ethylene oxide[9] at 0°, washed with acetone, and dried at 150°. Coverages calculated from C, H, N microanalysis by Miss H. Beck ranged between 1.30 and 1.60 molecules/nm^2 (1.29-1.45 mmol of N/g).

Characterization. The ir spectrum of the modified gel was recorded on a Beckman IR-5 spectrometer in the region 4000-800 cm^{-1} using the KBr disk technique. A silica-KBr disk was used as the reference. Absorption bands were observed at 3140 (w), 1570 (w), 1550 (w), 1220 (s), 1040 (s), and 930 (m) cm^{-1} which can be assigned to vibrations involving the imidazole group.[10] and at 2960 (w) cm^{-1} which corresponds to C-H stretching in the propyl groups.[11] These results accord with the presence of imidazole and of propyl groups on the surface.

Preparation of Adsorbents. All preparations of the iron complexes and absorbents were carried out in Schlenk-type glassware[12a] under an atmosphere of thoroughly deoxygenated and dried nitrogen. All solvents were saturated with nitrogen and transferred by syringe techniques.[12b]

The iron complexes,[13] $Fe(TPP)(py)_2$[14] and $Fe(TPP)(pip)_2$.[15] were prepared by literature methods and were characterized by satisfactory C, H, N analyses and by their visible spectra.[14]

A typical adsorbent was prepared by adding 30 cm^3 of solvent to a 100-cm^3 Airless-Ware flask containing 50-60 mg of the iron complex and 1 g of the modified silica gel. Benzene or methylene chloride was the solvent for $Fe(TPP)(py)_2$, and 1% piperidine-methylene chloride (v/v) for $Fe(TPP)(pip)_2$. The mixture was

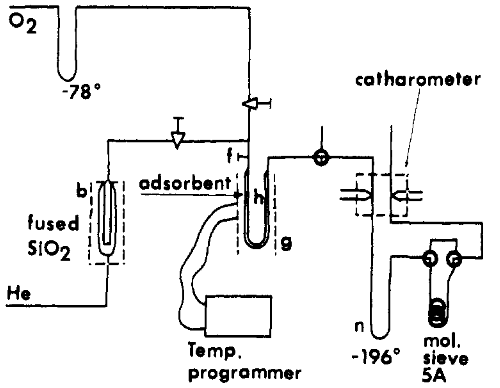


Figure 1. Apparatus for adsorption experiments.

stirred at room temperature for 3 hr; the supernatant liquid was then decanted. The resulting solid was washed with four 10-cm^3 portions of solvent, and then was dried in vacuo.

The adsorbents were analyzed for iron spectrophotometrically with 1,10-phenanthroline, after digestion with nitric and sulfuric acids.[16]

Apparatus. The apparatus used in the adsorption experiments is shown schematically in Figure 1. Helium, purified by permeation through fused silica at 400° using the device manufactured by Electron Technology, Kearny, N.J. (b), was passed at 60 cm^3 min^{-1} over the adsorbent at h. The flow then went to one arm of the catharometer (thermal conductivity cell) and then through the silica gel trap, n, which when cooled to $-196°$ adsorbed oxygen and other gases from the helium stream. Upon warming the trap, the oxygen (and other gases) was released as a pulse which passed through the column of molecular sieves 5A so as to provide a retention time for purposes of identification and then through the second arm of the catharometer. The flow rate was measured at the exit by a soap bubble flowmeter.

The adsorbent was activated by heating in flowing helium using the furnace, g. Pulses of various gases could be injected through the septum, f. Adsorption experiments at $-127°$ used a methylcyclohexane-liquid nitrogen slush bath.[12c] The temperature was monitored with an iron-Constantan thermocouple.

In a typical experiment, the modified silica was activated at 250° for about 3 hr, cooled to $-127°$, exposed to dry oxygen for 2 min, and flushed with helium for 10 min. The adsorbent was then allowed to warm to room temperature. The liberated oxygen gave a broad negative peak as it passed the first arm of the catharometer and it was then adsorbed in the trap, n. Warming the trap liberated the oxygen as a sharp peak which passed the molecular sieve column and then the second arm of the catharometer. The area of the peak observed here gave the amount of oxygen originally adsorbed by the modified silica gel.

Adsorption isotherms of oxygen on several iron-containing gels were determined on a volumetric apparatus which used a Kistler Instrument Co. Series 314 servo pressure sensor provided with data conditioning equipment giving a digital output. We are indebted to Mr. R. J. Loyd of this department for designing this equipment. Dead spaces were determined by helium.

Results

Oxygen at $-127°$ exhibits a phenomenon which we had not observed in our previous studies of adsorption of other gases at higher temperatures on various modified silica gels,[7,8] irreversible physical adsorption. Thus, various preparations of IPG (imidazolylpropyl gel) without attached iron porphyrin exhibited irreversible adsorption of between 0.0066 and 0.0078 mmol g^{-1} of oxygen. An IPG with the latter value of irreversible adsorption was treated with methanol at 168° to methoxylate the surface silanol groups. This reduced the value but only to 0.0060. The original unmodified silica gel gave the same value. Observed adsorptions of oxygen on IPG with iron porphyrin were corrected by the values for the IPG alone.

As shown in Table I, the amount of irreversibly adsorbed oxygen increased with the temperature of activation and with the time at a given temperature. Activation at 250° for 3 hr seemed to produce full activation. No visible sign of extensive decomposition was observed during this activation, but a small amount of colorless liquid (apparently either pyridine or piperidine) condensed at the outlet from the adsorbent bed and there was some darkening of the solid. At 320° there was definite evidence for decomposition of the material attached to the silica gel.

Table I. Effect of the Temperature of Pretreatment upon the Amount of Irreversible Chemisorption of Oxygen at $-127°$

Temperature of activation, °C	Time of activation, hr	Adsorption,[a] cm^3 g^{-1}
110	1	0.30
180	1	0.41
250	0.75	0.51
250	3	0.60
280	3.5	0.60

[a] On 0.468 g of Fe(TPP)pip(IPG) which contained 0.0181 mmol of Fe/g. The observed adsorptions are uncorrected for the blank, but expressed per gram of adsorbent.

Table II. Chemisorption of Oxygen Irreversible at $-127°$ on Silica Gels Modified with Fe(TPP)

Gel[a]	Activation °C	hr	Adsorption,[b] mmol g^{-1}	Fe, mmol g^{-1}
Fe(TPP)pip(IPG)	*250*	*3*	*0.0180*	*0.0181*
Fe(TPP)pip(IPG)	250	3	0.0184	0.0181
Fe(TPP)py(IPG)	260	2	0.0089	0.0100
Fe(TPP)py(IPG)[c,d]	250	2	0.0128	0.0130
Fe(TPP)py(IPG)[e]	240	1	0.0164	0.0324
Fe(TPP)py(IPG)[d]	270	1	0.0120	0.0229

[a] The symbol signifies *meso*-tetraphenylporphyrin(piperidine or pyridine)(imidazolylpropylsilica)iron(II). [b] After subtraction of the blank. [c] A 20-nm pore diameter silica was used here. [d] Benzene was used as the solvent for Fe(TPP)(py)$_2$. In the other listed runs, dichloromethane was used. [e] The IPG was treated with methanol vapor at 168° before exposure to Fe(TPP)(py)$_2$.

Table II lists the irreversible chemisorptions of oxygen on the various preparations. All standard preparations gave a ratio of oxygen uptake to content in iron which was very near unity. Because of the large blank, about 30% of the total adsorption, we tried to increase the amount of iron porphyrin on the gel. Since the diameter of the tetraphenylporphyrin molecule is about 1.8 nm, since there were about 1.4 imidazole groups per square nanometer, one might expect to be able to attach nearly 0.25 molecules of tetraphenylporphyrin per square nanometer. The observed degree of attachment was only about 0.1 of this value. Since this low value might result from steric restrictions in the pore structure of silica gel (which is like that of a loose gravel bed) we made a preparation on a silica gel with a larger pore diameter, about 20 nm. This gel was similar to Davison grade 952 except for a larger mesh size. We are indebted to Stanley M. Brown of W. R. Grace for supplying this material. However, as shown in Table II, this gel gave the same results as Davison grade 59.

It was conceivable that the low coverage resulted from deactivation of the imidazole groups by hydrogen bonding to surface silanol groups. Accordingly, surface silanol groups were converted to surface methoxy groups by treatment of IPG with methanol vapor at 168° before exposure to Fe(TPP)L$_2$. There was an increase in the degree of attachment of Fe(TPP) as shown in Table II, but none in the amount of oxygen adsorbed. The origin of this result is unknown.

The nature of the blank and its correctness were con-

Table III. Effect of Adsorption of Ammonia upon the Subsequent Chemisorption of Oxygen at −127°

Adsorbent	Adsorption[a]	
	$cm^3\ g^{-1}$	$mmol\ g^{-1}$
IPG[b]	0.19	0.0078
Fe(TPP)py(IPG)[c]	0.19	0.0078
150° for 2 hr[d]	0.29	0.0119
250° for 4 hr[e]	0.43	0.0175
NH_3 at 0°[f]	0.17	0.0072
273° for 2 hr[e]	0.47	0.0192

[a] Observed measurement at −127° uncorrected for blank. [b] Before exposure to $Fe(TPP)(py)_2$. [c] The sample containing 0.0130 mmol of Fe g^{-1}, Table II, after flushing with helium for 1.5 hr at 25°. [d] A sample containing 0.0229 mmol of Fe g^{-1} after the listed activation. [e] The preceding sample was reactivated as shown. [f] With 10 cm^3 of NH_3(g) passed over the preceding sample at 0° and flushed with helium.

firmed by poisoning the adsorbent with ammonia at 0° and determining the amount of physisorption irreversible at −127° on this material. As shown in Table III, the value was 0.0072 mmol g^{-1}, a value indistinguishable to within the experimental error from the irreversible physisorption observed on IPG before attachment of Fe(TPP), 0.0078. Poisoning by piperidine led to an adsorption of 0.0078.

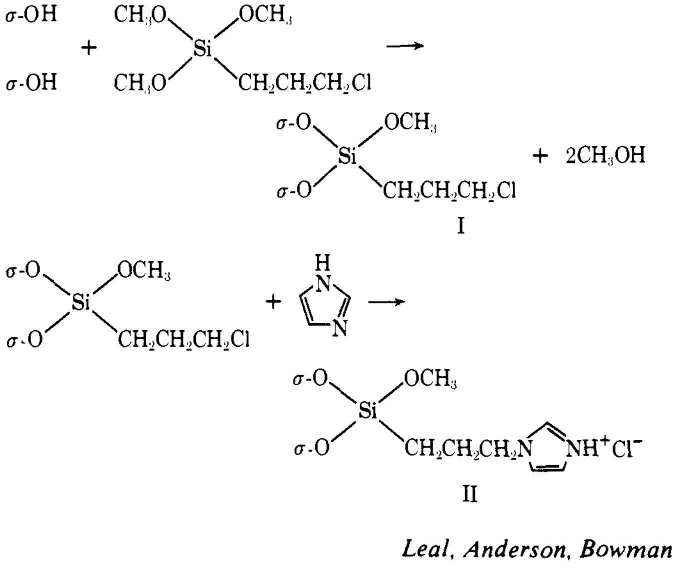
The activated adsorbent adsorbs carbon monoxide much more strongly than oxygen. Thus, the adsorbent was exposed to carbon monoxide for 2 min at 25° and purged with helium for 10 min. When the temperature of the adsorbent was raised to 160° by the temperature programmer, a volume of carbon monoxide was liberated which agreed well with that of irreversible oxygen chemisorption at −127°.

Figure 2 shows adsorption isotherms at −78 and 0° measured on 3.25 g of Fe(TPP)py(IPG) which contained 0.0229 mmol of Fe per gram of gel. The gel was activated to remove the residual pyridine by evacuation for 3.5 hr at 250°, the −78° isotherm was run, the gel warmed to 25° and evacuated, and another −78° isotherm run. The original isotherm was nearly exactly duplicated. The 0° isotherm was then run. Following that, the sample was exposed to ammonia gas for 10 min and flushed with helium. The 0 and −78° isotherms labeled "deactivated" were then run. Evacuation at 185° for 1 hr restored only two-thirds of the original capacity measured at −78°, but subsequent evacuation at 250° for 1.5 hr nearly completely restored the capacity as shown by the circles in the figure.

Discussion

The preparation of compound II below can be run in two successive steps (Scheme I),[7]

Scheme I



I

II

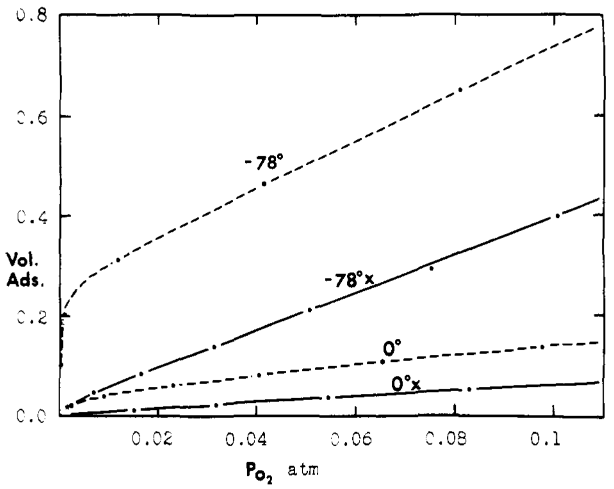
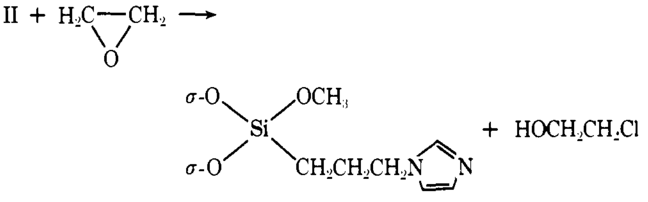


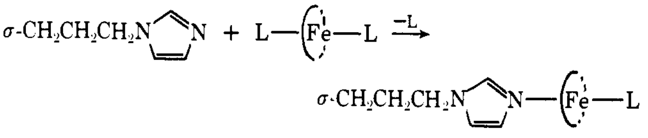
Figure 2. Adsorption of dioxygen in cubic centimeters (STP) per gram at −78 and 0° on Fe(TPP)(IPG) prepared by activation of Fe(TPP)py(IPG) (filled circles) and after deactivation with ammonia to form $Fe(TPP)(NH_3)$(IPG) (stars, × added to temperature).

where σ represents a silicon atom at the surface of silica gel. In addition, the reaction can be run in one step by adding a mixture of the silane and imidazole. Our coverages of between 1.3 and 1.6 imidazole groups per square nanometer use somewhat more than half of the five silanol groups per square nanometer of the surface of silica gel if, as seems probable,[7] the silane is diattached to the surface as shown. The reaction, in effect, merely extends the primary particles of the silica gel by one layer and it provides surface silicon atoms with attached organic groups. The imidazole hydrochloride(II) can be dehydrochlorinated by treatment with ethylene oxide at 0° to give IPG.



IPG

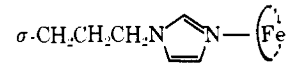
Several lines of evidence indicate that IPG reacts with $Fe(TPP)L_2$ to form Fe(TPP)L(IPG).



Fe(TPP)L(IPG)

In our experiments, L was either pyridine or piperidine. The visible absorption spectrum of Fe(TPP)L(IPG) immersed in heptane[17] exhibited a band centered at 532 nm characteristic of bis(base)tetraphenylporphyriniron(II).[14]

Heating Fe(TPP)L(IPG) at 250° in flowing helium generates the active adsorbent apparently by loss of the remaining L to form a species containing coordinatively unsaturated surface (cus) iron.



Fe(TPP)(IPG)

Such a species would resemble the active sites of hemoglobin and myoglobin which are known to involve a five-coordinate iron(II) porphyrin complex with the imidazole portion of a histidine residue occupying the fifth coordination

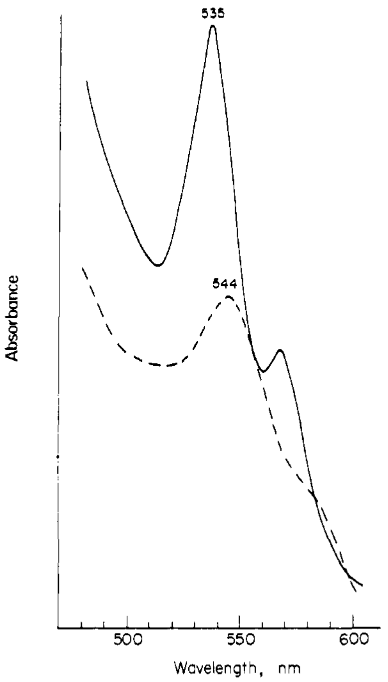
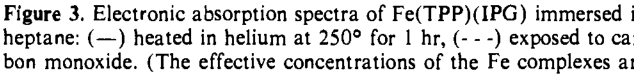


Figure 3. Electronic absorption spectra of Fe(TPP)(IPG) immersed in heptane: (—) heated in helium at 250° for 1 hr, (- - -) exposed to carbon monoxide. (The effective concentrations of the Fe complexes are similar but not identical.)

position. The open coordination site can then reversibly bind dioxygen.



Fe(TPP)(IPG)O_2

However, study of adsorption by the apparatus of Figure 1 requires that the oxygen adsorb at some temperature at which desorption in flowing helium occurs with a negligible rate. Thus very low temperatures are required in order to prevent the reaction.

$$\mathrm{Fe(TPP)(IPG)O_2} \longrightarrow \mathrm{Fe(TPP)(IPG)} + \mathrm{O_2(g)}$$

We have used −127° as a convenient temperature, but temperatures much higher could not be used. In desorption, the adsorbed oxygen is completely evolved by −78° and irreversibly chemisorbed oxygen is negligible in runs at −78°. Adsorption at −127° is a little slow. The surface is saturated in a 2-min exposure to oxygen but not much oxygen is adsorbed from a pulse about 6 sec wide.

As shown in Table II, several preparations gave a ratio (O_2 adsorbed irreversibly at −127°)/(content in Fe) of nearly unity which indicates that each atom of Fe adsorbs one molecule of oxygen. Even after six adsorption-desorption cycles, the amount of oxygen irreversibly adsorbed at −127° was unchanged. However, prolonged contact with air at room temperature led to a reduction of irreversible oxygen chemisorption at −127° but activation at 250° fully regenerated the adsorptive capacity, presumably by desorption of water adsorbed from the air. Thus, the attached iron porphyrin shows no tendencies toward irreversible formation of $\mathrm{Fe^{III}}$-O-$\mathrm{Fe^{III}}$.

In view of the relatively large correction for irreversible physisorption needed in the measurement of the chemisorption of oxygen at −127°, we also measured adsorption isotherms at higher temperatures so as to provide an independent measurement of the extent of oxygen chemisorption. The isotherm at −78° in Figure 2 shows strong adsorption of oxygen which is nearly saturated by 0.01 atm followed by physisorption which approximately follows Henry's law. The strong chemisorption would clearly become irreversible at lower temperatures. Exposure of the adsorbent to ammonia eliminates the chemisorption with little effect upon the physisorption. The difference between the linear portions of curves −78° and −78°X extrapolated to zero pressure must be the chemisorption and it amounts to 0.25 $\mathrm{cm^3\ g^{-1}}$ or 0.011 mmol $\mathrm{g^{-1}}$, which is in good agreement with the value obtained at −127°, 0.012 mmol $\mathrm{g^{-1}}$ (last line of Table II). Data at higher pressures than shown in Figure 1 for the poisoned and unpoisoned runs at 0° indicate than an oxygen pressure of 0.3 atm would be needed to convert one-half of the Fe(TPP)(IPG) to Fe(TPP)(IPG)O_2 at 0°.

Our data indicate that at −127° there is an irreversible physisorption of oxygen which is nearly the same on bare silica, on PIG, on Fe(TPP)(IPG)L, and on Fe(TPP)(IPG)NH_3. The conclusion that this is physisorption is supported by the observation that both nitrogen and argon give similar irreversible adsorptions, but in an amount which declines as the boiling point of the gas declines. Presumably the strong physisorption is located in the most favorable micropores.

The gel IPG bound $\mathrm{Fe^{III}}$(TPP)Cl to about the same extent as it bound Fe(TPP)L_2. The nature of binding of the Fe(III) complex was not examined in detail but the gel gave no increase in irreversible adsorption of oxygen at −127° over that of the blanks. We suggest, in those cases in which the moles of bound oxygen were less than those of iron, that there had been oxidation of the Fe(II) porphyrin during its preparation.

The adsorptive capacity of Fe(TPP)(IPG) for carbon monoxide is the same as that for oxygen, but carbon monoxide is held much more strongly than oxygen; Fe(TPP)(IGP)(CO) does not dissociate significantly at 0°. This result parallels the stronger binding of carbon monoxide than of oxygen on hemoglobin and myoglobin.[18] The same effect has been found in the binding of oxygen and carbon monoxide to Fe(TPP)(1-methylimidazole) in methylene chloride solution at −79°.[19] The visible absorption spectrum of the carbon monoxide adduct immersed in heptane[17] is shown in Figure 3. The band at 544 nm and the shoulder at 580 nm correspond to absorption bands at 543 and 581 nm exhibited by Fe(TPP)(1-methylimidazole)CO in solution in methylene chloride.

We conclude that we have prepared an adsorbent of the formula Fe(TPP)(IPG) which chemisorbs one oxygen molecule on each atom of iron, and which is not destroyed by exposure to oxygen at room temperatures and probably considerably above. The resistance to formation of μ-oxo dimer, $\mathrm{Fe^{III}}$-O-$\mathrm{Fe^{III}}$, appears to result from motional hindrance occasioned by attachment of the Fe(TPP) portion to the rigid surface of silica. The chemisorption of oxygen is a weak one by ordinary standards. It is irreversible at −127°, the coverage is one-half at very roughly 0.4 Torr ($P_{1/2}$ = 0.4 Torr). At 0°, $P_{1/2}$ is about 230 Torr and at −46°, 4 Torr (from data on another preparation than that of Figure 1).

Myoglobin in aqueous solution adsorbs oxygen more strongly than does this modified silica gel. Data for human myoglobin extrapolated to 0° give $P_{1/2}$ as 0.14 Torr,[20] for sperm whale myoglobin, 0.08 Torr.[18] About a factor of ten in the difference may result from our use of tetraphenylporphyrin, since in toluene solution at −45°, $P_{1/2}$ = 69 Torr for $\mathrm{Co^{2+}}$ bonded to the dimethyl ester of protoporphyrin IX and imidazole whereas $P_{1/2}$ of the analogous complex with tetraphenylporphyrin is 631 Torr.[21] The $\mathrm{Fe^{II}}$(pyrroheme) with a pyridine tail of Traylor at −45° gives $P_{1/2}$ = 400 Torr in toluene and 5 Torr in dimethylformamide.[22] At −45° in toluene, the ratio of $P_{1/2}$ for Co(II) (dimethyl ester of protoporphyrin IX) bonded to 1-methylimidazole to that bonded to pyridine is 0.07.[23] Thus, the iron porphyrin with a 1-alkylimidazole tail of the Traylor type might be expected to have $P_{1/2}$ of about 28 Torr in toluene at −45°. If the same type of porphyrin and 1-alkylimidazole ligand were used in all of the iron porphyrin complexes, the values for $P_{1/2}$ would probably fall within a factor of 100 or ΔG would fall in a range of 2.0–2.5 kcal mol^{-1}. Considering the complications introduced by solvation and possible effects of protein upon the stability of the oxygen complex of myoglobin, the agreement is probably as good as one can expect.

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(13) The following abbreviations will be used throughout this paper: Fe(TPP), *meso*-tetraphenylporphyriniron(II); $Fe(TPP)(py)_2$, *meso*-tetraphenylporphyrinbis(pyridine)iron(II); $Fe(TPP)(pip)_2$, *meso*-tetraphenylporphyrinbis(piperidine)iron(II); IPG, imidazolylpropyl gel.
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Synthesis and Properties of Osmium(II) and Osmium(III) Ammine Complexes of Aromatic Nitrogen Heterocyclics

Roy H. Magnuson and Henry Taube*

Contribution from Department of Chemistry, Stanford University, Stanford, California 94305. *Received December 28, 1974*

Abstract: Osmium(II) complexes of the type $[(NH_3)_4Os(N_2)(L)]^{n+}$, L = pyrazine, *N*-methylpyrazinium, isonicotinamide, isonicotinic acid, have been prepared by reaction of the appropriate nitrogen heterocycle with the bis(dinitrogen)tetraammineosmium(II) ion under argon. Heating of the dinitrogen(heterocycle)tetraammineosmium(II) ions in hydrohalic acids in air led to the isolation of osmium(III) compounds with the general formula $[(NH_3)_4Os(X)(L)]X_2$ for L = pyrazine, $X^- = Cl^-$, Br^-; and L = isonicotinic acid, $X^- = Cl^-$. Reduction of the osmium(III) ions resulted in the formation of the corresponding osmium(II) ions in solution. The pK_a of the chloro(pyrazinium)tetraammineosmium ion was found to be 7.6, seven orders of magnitude more basic than both the free ligand and the dinitrogen(pyrazine)tetraammineosmium(II) ion, and is indicative of very large back-bonding from the osmium(II) center to the nitrogen heterocycle. Anomalies in the charge transfer spectral bands of these ions are discussed in terms of a simple molecular orbital description and parameters of the back-bonding interaction, including the π-stabilization energy, are estimated. The ground state wave function of the pyrazinium osmium(II) π bond is found to possess greater ligand than metal character.

Complexes of ruthenium(III) and ruthenium(II) ammines with such ligands as pyridine and pyrazine have provided the basis for a wide variety of studies of substitution processes, electron transfer reactions, simple mixed-valence systems, and back-bonding interactions.[1–5] Displacement of a dinitrogen ligand has been used previously as a synthetic route to lower valence osmium ammine complexes.[6,7] In the course of our studies,[8] it was discovered that the *cis*-bis(dinitrogen)tetraammineosmium(II) ion[9] serves as a starting material for the introduction of an aromatic nitrogen heterocycle into the Os(II) coordination sphere. In this paper we report the preparation of a number of dinitrogen(N-heterocycle)tetraammineosmium(II) compounds, from which halogenotetraammineosmium(III) and chlorotetraammineosmium(II) complexes of pyrazine and isonicotinic acid are derived. A simple molecular orbital (MO) model has been applied to the π interaction in related Ru(II) compounds.[5] A similar approach is used here to discuss the unusual physical and spectral properties of the chlorotetraammineosmium(II) complexes in an effort to assess the back-bonding capability of this third-row transition metal.

Experimental Section

Materials and Reagents. Reagent grade chemicals were used throughout with the following exceptions: silver(I) *p*-toluenesulfonate, isonicotinic acid, pyrazine, chloroacetic acid, and hydrazine