First-order plots of ln ($A_t - A_\infty$) against time were linear to at least 3 half-lives and gave rate constants k_{obsd} (Table I), which exhibit a first-order dependence on [H_2O_2]. No dependence on pH was observed over the range pH 6.3–9.5 investigated, consistent with H_2O_2 (pK_a 11.67)[20] being the sole reactant. At 25 °C, k was found to be 5.5 ± 0.2 $M^{-1}\ s^{-1}$ in good agreement with the value previously reported (6.6 $M^{-1}\ s^{-1}$).[19] From the temperature dependence $\Delta H^\ddagger = 7.6 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = -2.9 \pm 2.0$ cal K^{-1} mol^{-1}. These values compare with $\Delta H^\ddagger = 4$ kcal mol^{-1} and $\Delta S^\ddagger = -11$ cal K^{-1} mol^{-1} for the reaction of deoxyHr with O_2.[14] The higher $\Delta H^\ddagger$ value is consistent with more extensive structural changes in the case of the H_2O_2 reaction. In support of the pH independence of rate constants Bradič et al. have reported that the protonated forms of NCO^-, N_3^-, and F^- are involved in complexation reactions with deoxyHr.[21]

Of particular interest is the formation of hydroxomet, D, characterized by two absorbance maxima in the 300–400-nm region at pH 6.3 as well as at pH 8.3. Subsequent absorbance changes corresponding to the D → C conversion are not as rapid or complete as we would at first have expected, which may be related to the recently proposed existance of cis and trans hydroxo forms.[11b] In a duplicate experiment in which D was generated by an alternative route and the pH then adjusted from 8.2 to 6.3, comparable absorbance time changes were observed. Also changes are not as well defined as we would like for the whole process since some denaturation of Hr occurs at the higher [H_2O_2] required to separate the two kinetic stages. It is possible that spectra reported previously[19] differ from those in the present work due to such denaturation, which is difficult to avoid at pH 6.3. At pH 8.3 a further slow reaction of D with H_2O_2 (0.12 M) is also observed with decay of absorbance bands in the 300–400-nm region in a first-order process, $t_{1/2} \approx 2$ h. This probably corresponds to denaturation as observed with $[IrCl_6]^{2-}$ and $[Mn(Cydta)(H_2O)]^-$ as oxidants[22] and in other studies described by Harrington and Wilkins.[23,24] In contrast to the earlier work[19] spectra similar to that of oxyHr were not observed. Since deoxyHr, A, is μ-hydroxo (or a closely related form) and metHr is μ-oxo, the $H_2O_2 \rightarrow 2OH^-$ change can be represented as in (4), with release of H_2O and retention of coordinated OH^- as in structure D.

$$\text{deoxyHr}(\mu\text{-OH}) + H_2O_2 \rightarrow \text{metHr(OH)}(\mu\text{-O}) + H_2O \qquad (4)$$

A very much slower uniphasic first-order process is observed in the oxidation of deoxyHr by BrO_4^- (3.3–13.3 mM) at pH 6.1–6.6. Rate constants k_{obsd} are independent of [BrO_4^-] and first order in [H^+], giving a second-order rate constant $k_H = (1.1 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$, and metHr (C) with a peak at 345 nm is formed. A similar process is observed with BrO_3^- (3.3–13.3 mM), $k_H \approx 21\ M^{-1}\ s^{-1}$. Both processes (25 °C; $I = 0.15$ M Na_2SO_4) therefore display characteristics previously identified by Wilkins and colleagues[21a] and assigned to the slow anion-catalyzed conversion of deoxyHr to metHr in the presence of traces of O_2.

To further test the 2e redox capability of the Hr active site, we investigated the reduction of metHr (10^{-5} M) with (1–3) × 10^{-5} M 2[4Fe-4S] in the fully reduced state (rr) at 25 °C, pH 6.3, and $I = 0.15$ M (Na_2SO_4). Consumption of reductant was monitored at 420 nm, ϵ for 2[4Fe-4S] (rr) being $2.7 \times 10^4\ M^{-1}\ cm^{-1}$, for the fully oxidized form (oo) $1.1 \times 10^4\ M^{-1}\ cm^{-1}$, and for the half-oxidized (or) midway between these values. At this wavelength the Hr absorbance contributes <5% to the total change. From an average of 10 determinations one electron (0.95 ± 0.08) was consumed per metHr, corresponding to formation of an $Fe^{II}Fe^{III}$ semimetHr form. Further slow reduction of this semimet product was not studied due to the extreme sensitivity of reduced 2[4Fe-4S] to traces of O_2 over long periods. It can be concluded that reaction occurs in 1e steps and there is no direct 2e conversion of Fe(II, II) to Fe(III, III).

It is clear that the specificity of the Hr active site for O_2 is linked to the 2e change $Fe^{II}_2 \rightarrow Fe^{III}_2$ and the availability of a proton from the OH^- bridging the two Fe(II)'s in A to give B. Almost accidentally H_2O_2 is able to utilize these same features in the 2e change $H_2O_2 \rightarrow 2OH^-$, with concomitant uptake of a proton from the bridging OH^- and formation of (bound) OH^- and (unbound) H_2O. With BrO_4^- and BrO_3^- as oxidants for deoxyHr the reactions proceed by alternative routes. Schematically 2e changes are possible, but these require inner-sphere O atom transfer, the implication of our results seems to be that neither of these reactants gains access to the active site due to their charge and/or size. With the 2[4Fe-4S] ferredoxin (reduction potential −400 mV)[25] access to the active site is not even a remote possibility, and no 2e reduction is observed. A direct 2e reduction of the met active site would probably require proton donation to the μ-O bridging ligand, which in this instance is more difficult to achieve.

Overall the Hr active site appears to be highly specific for a 2e change, which may be linked to the ability of the redox partner to accept/donate a proton from the bridge. Studies to date have shown that in contrast reactions of Hr with 1e redox reagents are extremely complex. A notable exception (which we do not fully understand) is the reaction with deoxymyoglobin, which accomplishes reduction of metHr in a single step.[26] The specificity of deoxyHr for neutral molecules is noted, and the observation that metHr will bind only small and/or linear anions such as OH^-, N_3^-, and NCS^- is of interest. We also note that the O_2^{2-} in oxyHr is bound in a bent (end-on) fashion, B, whereas CO, which binds in a linear manner to deoxyhemoglobin (and binds also to hemocyanin), does not bind to deoxyHr.[27]

Acknowledgment. We thank the U.K. Science and Engineering Research Council for a studentship (to G.D.A.).

Registry No. H_2O_2, 7722-84-1; BrO_4^-, 16474-32-1; BrO_3^-, 15541-45-4; O_2, 7782-44-7.

---

(20) Carpeni, G.; Haladjian, J.; Poize, S. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*, 733.

(21) (a) Bradič, Z.; Conrad, R.; Wilkins, R. G. *J. Biol. Chem.* **1977**, *252*, 6069. (b) Unpublished work in: Bradič, Z.; Tsukahara, K.; Wilkins, P. C.; Wilkins, R. G. In *Frontiers in Bioinorganic Chemistry*; Xavier, A. V., Ed.; VCH: Weinheim, FRG, 1986; p 340.

(22) Unpublished results; Cydta = 1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetate.

(23) Harrington, P. C.; Wilkins, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1550.

(24) Bradič, Z.; Harrington, P. C.; Wilkins, R. B.; Yoneda, G. *Biochemistry* **1980**, *19*, 4149.

(25) Stombaugh, N. A.; Sundquist, J. E.; Burns, R. H.; Orme-Johnson, W. H. *Biochemistry* **1976**, *15*, 2633.

(26) Bradič, Z.; Harrington, P. C.; Wilkins, R. G. *Biochemistry* **1979**, *18*, 889.

(27) Collman, J. P.; Brauman, J. I.; Halbert, T. R.; Suslick, K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3333.

Contribution from the Department of Environmental Sciences
and Engineering and Department of Chemistry,
University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27514

Preparation and Characterization of the μ-Oxo Dimer and Hydroxo Complexes of (Tetrakis(pentafluorophenyl)porphinato)iron(III)

K. Jayaraj, A. Gold,* G. E. Toney, J. H. Helms,
and W. E. Hatfield

Received March 21, 1986

On oxidation of ferrous tetraphenylporphyrin complexes with dioxygen or metathesis of the chloro ferric complexes with hydroxide,[1–6] bulky substituents such as methyl, methoxy, or ethoxy,

---

* To whom correspondence should be addressed at the Department of Environmental Sciences and Engineering.

(1) Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; LaMar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779.

(2) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884.

(3) Cheng, R.-J.; Latos-Grazynski, L.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 2412.

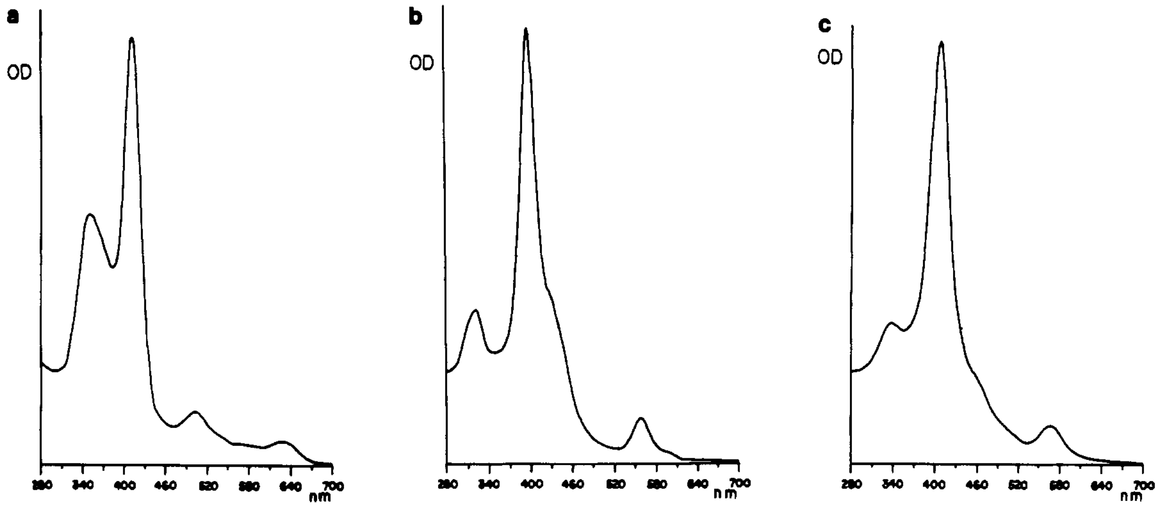

Figure 1. UV–vis (methylene chloride): (a) chloro(tetrakis(pentafluorophenyl)porphinato)iron(III); (b) μ-oxo dimer; (c) hydroxo complex.

or chlorine at the phenyl 2,6-positions result in isolation of the corresponding (hydroxo)(porphinato)iron(III) compounds as ultimate products. However, similar treatment of complexes with somewhat relaxed steric constraints, such as 3,4,5-trimethoxyphenyl- or pentafluorophenyl-substituted porphyrins,[3,7] has been reported to yield mixtures of hydroxo and μ-oxo species. These complexes are related by the reaction

$$2\mathrm{PFeOH} \rightleftharpoons \mathrm{PFeOFeP} + \mathrm{H_2O}$$

but in the two examples cited[3] the equilibrium was not forced in either direction nor were pure components separated from reaction mixtures. We wish to report here the preparation, separation, and characterization of both the μ-oxo dimer and the hydroxo complexes of the ((pentafluorophenyl)porphinato)iron derivative, in which steric interactions of *o*-fluorines allow both monomer and dimer to exist as stable forms.

Results and Discussion

The μ-oxo dimer, uncontaminated with monomer impurities, can be obtained by metathesis in benzene with excess aqueous sodium hydroxide followed by chromatography of the reaction mixture over neutral alumina with benzene eluant. A small quantity of material remaining at the top of the alumina column could be eluted with methylene chloride and proved to be the hydroxo complex. Repeated chromatography of the purified μ-oxo dimer over neutral alumina yielded no additional monomer; hence, the column served only to separate the complexes and did not catalyze equilibration between monomer and dimer in the inevitable presence of trace water. However, the use of hydrocarbon eluant for purification appears to be critical since chlorocarbon eluants invariably resulted in traces of a high-spin monomeric contaminant (presumably chloride), which was clearly evident in the sharp increase in μ_{eff} at 77 K in temperature-dependent magnetic moment measurements[8] on the dimer prepared under these conditions.

Preparation of the hydroxo complex can also be accomplished by metathesis; however, in order to avoid concomitant formation of major amounts of μ-oxo dimer, it is necessary to displace a weakly coordinating anion such as nitrate or tosylate[9] with a stoichiometric amount of hydroxide. The hydroxo complex is purified by chromatography over neutral alumina with methylene chloride eluant, containing 5% acetone or methanol to minimize the volume for collection. The microcrystalline solid is obtained by evaporation of solvent at ambient temperature under a stream of nitrogen; evaporation of solvent with heating or vacuum produces significant amounts of μ-oxo dimer. The μ-oxo dimer also forms slowly on standing in solution (25% conversion overnight), but the solid hydroxo complex is stable at −20 °C.

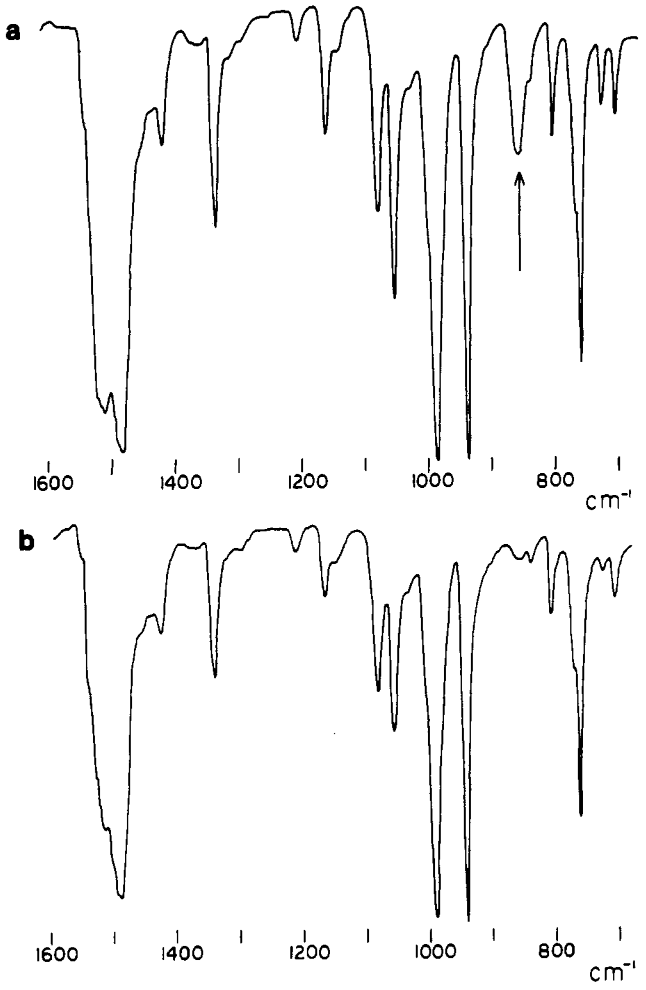

Figure 2. IR (KBr): (a) μ-oxo dimer of (tetrakis(pentafluorophenyl)porphinato)iron(III); (b) hydroxo complex. The arrow indicates the band at 850 cm^{-1} assigned to the Fe–O–Fe stretch of the μ-oxo dimer.

The properties of the μ-oxo dimer are consistent with those reported for other (μ-oxo)(porphinato)iron dimers.[10] The UV–vis

---

[4] Harel, Y.; Felton, R. H. *J. Chem. Soc., Chem. Commun.* **1984**, 206.

[5] Cense, J.-M.; LeQuan, R.-M. *Tetrahedron Lett.* **1979**, 3725.

[6] Gunter, M. J.; Mander, L. N.; Murray, K. S. *J. Chem. Soc., Chem. Commun.* **1981**, 799.

[7] Boersma, A. D.; Goff, H. M. *Inorg. Chim. Acta* **1984**, *89*, L49.

[8] Helms, J. H.; terHaar, L. W.; Hatfield, W. E.; Harris, D. L.; Jayaraj, K.; Toney, G. E.; Gold, A.; Mewborn, T. D.; Pemberton, J. E. *Inorg. Chem.* **1986**, *25*, 2334.

[9] Phillippi, M. A.; Baenziger, N.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 3904.

[10] Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1.

spectrum (Figure 1) is characteristic of oxyanionic complexes,[3,11,12] with the Soret band blue shifted relative to that of the chloro complex and lacking the splitting present in the spectrum of the chloro complex and with a β-band at 557 nm having a weak shoulder at 590 nm. The IR spectrum (Figure 2) shows a strong band at 850 cm^{-1} in the region expected for the Fe–O–Fe stretch.[10,12,13] The ^{1}H NMR spectrum consists of a single resonance at 13.9 ppm, peak width 0.32 ppm at half the peak height. The narrowed peak width compared to pyrrole signals of high-spin complexes is indicative of decreased paramagnetism[14] resulting from antiferromagnetic coupling of the ferric centers, which is evident in the solid-state magnetic moment, $\mu_{\text{eff}} = 1.6\ \mu_B$, at ambient temperature.

The similarity between the features of UV–vis spectra of μ-oxo and oxyanionic complexes generally observed for (porphinato)iron complexes[3,11] is also apparent in the case of the hydroxo pentafluorophenyl complex. The major distinction between the spectra of the μ-oxo dimer and the hydroxo complex is a red shift of both the Soret and β-bands of the hydroxo complex (Figure 1). ^{1}H NMR indicates that water molecules are associated with (hydroxo)((pentafluorophenyl)porphinato)iron(III); hence, the assignment of the hydroxo –OH stretch in the IR spectrum is ambiguous. The IR spectrum shows a prominent absorbance at 3400 cm^{-1}, with a shoulder at 3600 cm^{-1} in the region of –OH stretch. The absence of absorbance between 800 and 900 cm^{-1}, where the Fe–O–Fe stretch is expected[10] and is indeed present in the spectrum of the μ-oxo dimer, confirms the monomeric structure (Figure 2). In contrast to the case of the μ-oxo dimer, the ^{1}H NMR of the hydroxo complex shows a single broad pyrrole resonance at 82 ppm with a width of 3.5 ppm at peak half-height. A broad resonance at ~1.5 ppm is ascribed to the water solvate.[3] The chemical shift of the pyrrole proton is typical of high-spin *meso*-(tetraarylporphinato)iron(III) complexes,[15] and the $S = {}^5/_2$ spin state of iron is further supported by the $\mu_{\text{eff}} = 5.7\ \mu_B$ measured by the Evans method.[16] The EPR spectrum in frozen solution is also typical of axially symmetric high-spin (porphinato)iron(III),[17] showing a strong transition at $g_\perp = 5.9$ and a weaker signal at $g_\parallel = 2$. However, the intensity of the feature at $g = 2$ is higher relative to the $g_\perp$ transition than the $g = 2$ signal in the EPR spectrum of the chloro complex, in accord with observations reported for several other hydroxo compounds.[3]

(Tetrakis(pentafluorophenyl)porphinato)iron(III) is one of several sterically encumbered complexes that have been shown to form mixtures of monomeric hydroxo and dimeric μ-oxo derivatives. We have established conditions for the pentafluorophenyl complex under which each of the two forms will predominate, have developed a procedure for their separation by column chromatography, and have shown that they are sufficiently stable for characterization.

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained on a Bruker AC200 at 200 MHz. IR spectra were recorded in a KBr matrix on a Beckman 4250 spectrometer, and UV–vis spectra on a Coleman 124 double-beam spectrophotometer. EPR spectra were recorded in the X-band on a Varian E109 spectrometer in frozen methylene chloride solution at 77 K.

μ-Oxo Dimer. The pure μ-oxo dimer was obtained from the chloro complex or a mixture of μ-oxo dimer and chloro complex (from the metalation of the free base[18]) by dissolving 100 mg of the starting (porphinato)iron in 25 mL of methylene chloride and stirring 4 h with an equal volume of 2 N NaOH. The organic layer was separated, washed twice with water, dried over Na_2SO_4, and chromatographed over neutral alumina (Fisher, A540) with 1:1 benzene/hexane as eluant. The red band containing the μ-oxo dimer was collected and the solid (68 mg) obtained as dark red needles on slow evaporation of solvent. The magnetic moment determined in the solid state at ambient temperature is 1.6 μ_B. UV–vis (toluene) $\lambda_{\max}$ ($\epsilon \times 10^{-3}$): 393 (62.4), 557 (7.0), 590 sh nm. Anal. Calcd for $C_{88}H_{16}N_8F_{40}Fe_2O$: C, 50.97; H, 0.77; N, 5.41; Fe, 5.41. Found: C, 51.58; H, 1.47; N, 5.36; Fe, 5.00.

Hydroxo Complex. Fifty milligrams of μ-oxo dimer was dissolved in 15 mL of methylene chloride, and the solution, along with 0.2 mL of water and 75 mg of *p*-toluenesulfonic acid, was added to a separatory funnel and shaken with periodic monitoring by UV–vis spectroscopy until the spectrum of the sulfonato complex appeared: $\lambda_{\max}$ 350, 406, 510, 630 nm. The solution was dried over sodium sulfate and the solvent removed on a rotary evaporator. The residue was redissolved in 15 mL of methylene chloride and shaken in a separatory funnel with a stoichiometric amount of 1 N NaOH (0.1 mL) until the β-band of the hydroxo complex (563 nm) no longer changed. After the solution was dried over sodium sulfate, the solvent was removed under a stream of nitrogen and the residue chromatographed over alumina with methylene chloride containing 5% acetone or methanol as eluant. The hydroxo complex eluted slowly as a brownish band and was obtained as a solid on removal of solvent under a stream of nitrogen at ambient temperature. UV–vis (methylene chloride) $\lambda_{\max}$ ($\epsilon \times 10^{-3}$): 406 (76), 563 (11.9) nm. A satisfactory analysis of the hydroxo complex could not be obtained, presumably as a result of the inability to remove solvents completely by warming and/or vacuum without generating μ-oxo dimer.

Acknowledgment. This work was supported by USPHS Grant ES03433.

Registry No. ((Pentafluorophenyl)porphinato)iron(III) μ-oxo dimer, 81245-20-7; chloro((pentafluorophenyl)porphinato)iron(III), 36965-71-6; hydroxo((pentafluorophenyl)porphinato)iron(III), 81278-77-5; ((*p*-tolylsulfonyl)oxy)((pentafluorophenyl)porphinato)iron(III), 103500-01-2.

---

(11) Quinn, R.; Nappa, N.; Valentine, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 2588.

(12) Fleischer, E. B.; Srivastava, T. S. *J. Am. Chem. Soc.* **1969**, *91*, 2403.

(13) Burke, J. M.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 6077.

(14) LaMar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63.

(15) Goff, H. M. In *Iron Porphyrins*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, PA, 1983; Part 1, pp 237–273.

(16) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(17) Lin, W. C. In *The Porphyrins*; Dolphin, D. H., Ed.; Academic: New York, 1978; Vol. IV, Chapter 7.

(18) Adler, A. D.; Longo, F. R.; Kampus, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2442.

Contribution from the Department of Chemistry,
Arizona State University, Tempe, Arizona 85287

Electronegativity and Bonding of Transitional Elements

R. T. Sanderson*

Received January 10, 1986

Although numerous arbitrary evaluations of electronegativity of transitional elements have been published in most textbooks of inorganic chemistry, reliable evaluation has been prevented, until now, by lack of information concerning homonuclear bond energies and nonpolar covalent radii, especially for gaseous molecules, and by uncertainties concerning the effects of underlying incompletely filled d orbitals and electrons. This paper presents the results of an attempt to determine suitable electronegativity values for the transitional elements and to assess how these values relate to their polar covalent bonding.

Evaluation of Electronegativity

The quantitative theory of polar covalence[1-3] divides the total energy of a polar covalent bond into two contributions, a nonpolar covalent energy and an ionic energy. The total energy if the bond were nonpolar covalent, E_c, is simply the geometric mean of the two homonuclear single covalent bond energies, E_{AA} and E_{BB}, corrected for any difference between the actual bond length, R_o and the sum of the nonpolar covalent radii, R_c, by the factor R_c/R_o:

$$E_c = R_c(E_{AA}E_{BB})^{1/2}/R_o \qquad (1)$$

If the bond were ionic, the energy, E_i, would be the Coulombic energy between unlike unit charges at the observed internuclear distance:

---

* Address for correspondence: 4725 Player Drive, Fort Collins, CO 80525.