Sulfur reacted readily with PF_3 to give a 50% yield of SPF_3 at 800 atm and 300°. When the pressure was increased to 4000 atm, an almost quantitative conversion was obtained. The usefulness of high pressure to retard thermal decomposition is demonstrated by this work since Thorpe and Rodger, who carried out the first synthesis of SPF_3 from P_4S_{10} and PbF_2, found that this substance decomposed to sulfur and PF_3 at 300°.[16] Since the decomposition reaction requires an increase in volume as the reaction progresses, the decomposition would not be favored at high pressure.

The literature contains many references to the synthesis of OPF_3, including the low-pressure synthesis from O_2 and PF_3 in an electric discharge.[17] At pressures greater than 800 atm within 12 hr at 300°, PF_3 is converted to OPF_3 in approximately 90% yields. When the pressure is increased to 4000 atm, the yield is approximately the same, however, no reaction takes place at 4000 atm and 25°.

Phosphorus trifluoride and oxygen in the presence of magnesium at 4000 atm and 300° readily forms $[F_2P(O)]_2O$. This product is most likely formed by the reaction of OPF_3 and magnesium oxide. The magnesium oxide formation is not pressure dependent; however, as discussed earlier, the synthesis of OPF_3 requires high pressure.

$$2Mg + O_2 \rightarrow 2MgO \tag{3}$$

$$2PF_3 + O_2 \rightarrow 2OPF_3 \tag{4}$$

$$MgO + 2OPF_3 \rightarrow MgF_2 + P_2O_3F_4 \tag{5}$$

Magnesium and OPF_3 do not undergo reaction under similar conditions, and only traces of $P_2O_3F_4$ have been observed when these substances were combined. This is most likely due to a thin oxide film on the metal.[18]

The analogous reaction with sulfur, SPF_3, and magnesium does not take place.

Registry No. OPF_3, 13478-20-1; $[F_2PO]_2O$, 14456-60-1; SPF_3, 2404-52-6; PF_3, 7783-55-3; O_2, 7782-44-7; S, 7704-34-9; Se, 7782-49-2; Te, 13494-80-9; $SePF_3$, 26083-30-7.

Acknowledgment. This research was supported by the National Science Foundation under Grant GP-19873.

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Kinetics of Interaction of Nickel(II) with 2-(2-Aminoethyl)pyridine

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The reactivity of ligands containing nitrogen donor atoms toward transition metal ions in oxidation state II, particularly nickel(II), has been examined thoroughly.[2] When the ligand taking part in metal complex formation is uncharged, the mechanism of the formation process is in most cases well understood irrespective of the ligand dentate number. However, the nature of the variation of reaction rates encountered[2-4] when nickel(II) reacts with protonated ligands precludes the application of any simple unifying mechanistic scheme in this situation.

As a consequence, a study has been undertaken of the kinetics of reaction of nickel ions with certain mixed aromatic and aliphatic amines[5] which exist as a mixture of protonated and unprotonated forms in the neutral to weak acidic pH range. From these results and others, the importance in the complex formation process of ligand charge and chelate ring size, besides metal-ligand affinity, may be assessed. 2-(2-Aminoethyl)pyridine, AEP, reacts with nickel ions, and thermodynamic quantities for the formation of the six-membered chelate ring 1:1 and 1:2 complexes have been obtained.[6] This communication is concerned with the kinetics and mechanism of the 1:1 Ni(II)-AEP complex formation.

Experimental Section

Materials. 2-(2-Aminoethyl)pyridine (Aldrich) was distilled under vacuum and dissolved in absolute ethanol. Dry hydrogen chloride was bubbled through the stirred solution. The resulting precipitate was isolated under a nitrogen blanket and washed thoroughly with absolute ethanol. *Anal.* Calcd for $C_7H_{10}N_2 \cdot 2HCl$: C, 43.06; H, 6.20; N, 14.37. Found: C, 42.66; H, 6.25; N, 14.41. Reagent grade nickel nitrate was used as a source of nickel ions. The concentration of stock nickel solutions was estimated complexometrically. Other materials used were reagent grade commercial products.

Proton Dissociation Constants. Ligand solutions were titrated potentiometrically with standard sodium hydroxide solution to yield in separate determinations the two proton dissociation constants. The ionic strength of 0.1 *M* was achieved by addition of the appropriate amount of sodium perchlorate, and the measurements were made at 25°. The results obtained, pK_{a_1} of 3.82 ± 0.02 and pK_{a_2} of 9.65 ± 0.02, are consistent with values available by interpolation of literature data.[6]

Kinetics. The nickel complex of AEP has a higher absorbance than a mixture of the protonated and neutral forms of AEP in the ultraviolet region. Wavelengths used for monitoring complex formation in a Durrum-Gibson stopped-flow spectrophotometer were 275 nm (cacodylate buffer) and 288 nm (2,6-lutidine buffer). Reactions were run under pseudo-first-order conditions with nickel ion concentrations in the range 13-80-fold excess to ensure that only the 1:1 complex is formed. For most kinetic determinations both metal ion and ligand solutions were maintained at a desired pH with a buffering agent and the ionic strength of each solution was made up to 0.1 *M* with sodium perchlorate. A few measurements were made at pH just above 7. For these, in order to minimize any possible complication from precipitation of nickel hydroxide, the ligand solution was buffered with 0.02 *M* lutidine buffer (a concentration twice that used in experiments below pH 7) and mixed with unbuffered nickel ion solution below pH 7. The pH of the resulting mixture (total ionic strength of 0.1 *M*) was measured and is assumed to be obtained virtually within the mixing time of the stopped-flow instrument. Visual observation of the mixed solution and appropriate blank runs confirm that in the time after mixing in which kinetic measurements are made, about 10 sec, there is no apparent interference from formation of insoluble material. Oscilloscope traces yielded excellent first-order rate plots, linear for 3-4 half-lives. The pseudo-first-order rate constants were divided by the total nickel ion concentration to yield the second-order complex formation rate con-

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[1] National Science Foundation College Faculty Research Participant, 1971; on leave from Mt. Saint Mary's College, Emmitsburg, Md.

[2] (a) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. 49, 55 (1965); (b) R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

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stant, k_f. Values of k_f used in evaluating further parameters are in almost all cases an average of at least four individual determinations.

Results and Discussion

The reaction has been studied at several different total nickel ion concentrations in the range 2.5-16 mM and over the ligand concentration range 0.2-0.4 mM. The data are best described by an overall second-order reaction, first order in each reactant. The majority of reactions were run at 25.0°, although a few runs were carried out at other temperatures in the range 11-30°. Figure 1 is an illustration of the results obtained at 25.0° with initial conditions of $[Ni^{2+}] = 16$ mM and $[AEP] = 0.2$ mM. Two obvious features are the essential pH independence of the rate constant below pH 6 and the very pronounced pH sensitivity of the rate constant at the higher end of the range of measurement.

On the basis of the pK_a values of 9.65 for protonation of the primary nitrogen atom of AEP and 3.82 for protonation of the pyridine nitrogen atom, in the pH range of study, 5-7, the ligand is present predominantly in the monoprotonated form, $AEPH^+$, with much smaller amounts of $AEPH_2{}^{2+}$ and AEP present. Reaction between two species each of 2+ charge is likely to be very unfavorable. Consequently, it will be assumed that reaction of $AEPH_2{}^{2+}$ with the metal ion does not occur in these experiments. This assumption appears justified by the leveling off of k_f in the pH 5-6 range and by the subsequent analysis.

The rate of production of $Ni(AEP)^{2+}$ may then be written

$$d[Ni(AEP)^{2+}]/dt = k_f[Ni^{2+}][AEP]_{total} \qquad (1)$$

and also as

$$d[Ni(AEP)^{2+}]/dt = k_1[Ni^{2+}][AEP] + k_2[Ni^{2+}][AEPH^+] \qquad (2)$$

where the rate constants are defined in

$$Ni^{2+} + AEP \xrightarrow{k_1} Ni(AEP)^{2+} \qquad (3)$$

$$Ni^{2+} + AEPH^+ \xrightarrow{k_2} Ni(AEP)^{2+} + H^+ \qquad (4)$$

If the assumptions are made that proton liberation in reaction 4 is very rapid compared with the measurements made and that ligand forms are in very rapid equilibria with one another, then by substituting

$$K_{a_2} = [H^+][AEP]/[AEPH^+]$$

into (1) and (2) there results

$$k_f(1 + [H^+]/K_{a_2}]) = k_1 + k_2[H^+]/K_{a_2} \qquad (5)$$

Figure 2 is a plot of the left-hand side of (5) *vs.* $[H^+]/K_{a_2}$ at 25.0° from the data shown in Figure 1, and the line shown is the best line drawn through the points. From this graph, estimates of the individual rate constants are 7.3 M^{-1} sec^{-1} for k_2 and 9.5 × 10^3 M^{-1} sec^{-1} for k_1, at 25.0°. Because of the substantial difference in the pH sensitivity of the observed reaction in the range employed, the value of k_2 is considerably more precise than the value of k_1.

The value of k_1 indicates a high reactivity of AEP toward nickel ions, since many neutral nitrogen donor atom ligands in the absence of either steric retarding influence or rate-accelerating factors reacting with Ni(II) are characterized by rate constants in the range (1-6) × 10^3 M^{-1} sec^{-1}.[2] This suggests for the Ni^{2+}-AEP system a highly favorable value of K_o, the outer-sphere complex association constant, or, k_o, the rate constant for rate-determining water expulsion from the outer-sphere complex, the composite terms of k_1 ($k_1 = K_ok_o$).[2,7] Rate enhancements of this kind may be explained by invoking the internal conjugate base (ICB) mechanism[8,9-12] which accounts for increases in both terms. The magnitudes of the stabilization of the outer-sphere complex or the labilization of coordinated water molecule release appear to be dependent upon the basicity of a ligand nitrogen atom.[13] Therefore, in the absence of other differentiating features AEP (pK_a = 9.65) would be predicted to react more rapidly than the homologous amine 2-aminomethylpyridine, AMP (pK_a = 8.6[3]), with nickel ions. The fact that k_1 for AMP is 8.6 × 10^3 M^{-1} sec^{-1}, only marginally less than k_1 for AEP, suggests that a rate-retarding effect is superimposed upon any acceleration due to the ICB effect[14]

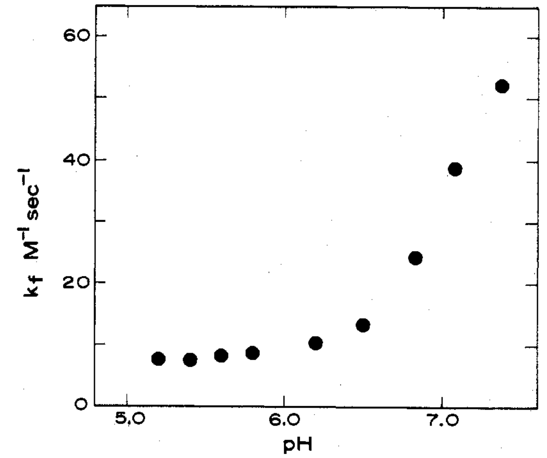

Figure 1. The pH dependence of k_f at 25.0° and $\mu = 0.1$ M for the formation of $Ni(AEP)^{2+}$.

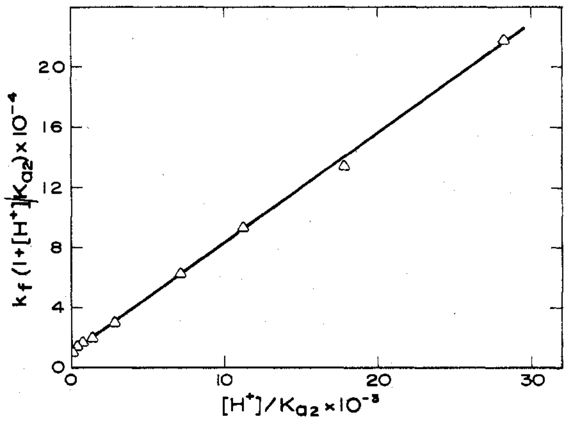

Figure 2. Plot of $k_f(1 + [H^+]/K_{a_2})$ *vs.* $[H^+]/K_{a_2}$ for the formation of $Ni(AEP)^{2+}$ at 25.0° and $\mu = 0.1$ M.

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(9) The formation of a hydrogen bond, essential to the ICB mechanism,[8] appears to be a reasonable hypothesis in a situation where the protonation constants for the aquonickel ion species and the ligand are similar. The exact nature of the metal ion species in neutral or weakly basic solution at the concentration levels employed here is not clear.[10-12]

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(13) D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969).

(14) Based upon the most recent estimation[4] of the theoretical value of k_1 for diamines, 8 × 10^3 M^{-1} sec^{-1}, the apparent ICB effect for AMP is virtually negligible and for AEP is only about a 12% enhancement. Use of two independent NH_3 molecules as a model in the calculation of K_o is probably satisfactory in this study since k_1 values for the reactions of Ni^{2+} with pyridine[2b] and with NH_3 are quite similar.

in the Ni^{2+}-AEP system. A possible source of this rate retardation is indicated when the results for reaction of protonated ligand forms are discussed below.

The reaction of $AEPH^+$ with Ni(II), characterized by a k_2 of 7.3 M^{-1} sec^{-1}, is slower than that of some other diamines; for example, k_2 for nickel ions reacting with enH^+ is approximately 50-fold larger (where en is ethylenediamine) but is of the same order as the reactions of $(N,N'\text{-}Et_2en)H^+$ and $phenH^+$–8.0[4] and ~2 M^{-1} sec^{-1},[15] respectively (phen is 1,10-phenanthroline)—yet a factor of 5 less than the values of 35 M^{-1} sec^{-1} for $AMPH^+$. A "theoretical" value of k_2 for enH^+ of 1.7×10^3 M^{-1} sec^{-1} has been proposed,[4] and steric effects and conformational changes have been employed to rationalize reductions from the theoretical value of experimental values for enH^+ and protonated *N*-alkyl-substituted derivatives of en. Because AEP forms a six-membered ring, the theoretical value of K_o' (the outer-sphere association constant for a protonated ligand) would be somewhat higher[16] since the protonated nitrogen atom will be further away from the nickel ion when $AEPH^+$ is the ligand compared with the model amine species used, enH^+. Consequently in the absence of other factors k_2 would be slightly higher. This is a relatively minor determinant and the effect is in the opposite direction to the observations. Sterically controlled substitution in the case of six-membered ring chelates usually manifests itself fully in metal ions where the metal ion coordinated water bonding is more labile than in the aquonickel ion,[17] although in the case of the formation of nickel(II) β-alanine, there is some evidence of involvement of chelate ring closure in the rate-determining step. The fact that $AMPH^+$ is considerably more reactive than $AEPH^+$ toward nickel ions while the corresponding neutral ligands react with Ni^{2+} at about the same rate suggests the involvement of steric control in the reaction of $AEPH^+$ (ignoring for the moment the ICB effect for the neutral ligands).

Since the ICB effect does not operate for protonated ligands, and if we may assume that the factor $k_2(AEPH^+)/k_2(AMPH^+) \approx 1:5$ is entirely due to sterically controlled substitution (steric hindrance due to the proton having to be removed from the primary nitrogen for chelation, should be similar in both ligands) and that this steric factor is similar for the corresponding neutral ligands, then it may be estimated that the apparent ICB effect, which is masked in the observed rate constants, is about fivefold for AEP over AMP. However, other factors may be involved since AMP itself does not appear to be significantly activated by an ICB process in its reaction with nickel.

The energy of activation for the reaction of $AEPH^+$ with nickel(II) ions has been determined from measurements of k_f at different temperatures and pH values in the range 11-30°. The value is about 18 kcal mol^{-1} which is larger than those values which characterize reaction[2a] of uncharged ligands with nickel(II). The uncertainty in determining k_1 prevents us from obtaining a reliable value for the energy of activation in the reaction of AEP with nickel(II) although the data show that it is considerably less than 18 kcal mol^{-1}.

Registry No. Nickel, 7440-02-0; 2-(2-aminoethyl)-pyridine, 2706-56-1.

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[15] Values cited in ref 2b.

[16] In contrast to K_o. Values of K_o for interaction of nickel ions with AMP and AEP should be very similar, excluding the ICB enhancement effect.

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Reaction of Dimethylketene with Cobalt Carbonyl

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Recently, metal-coordinated diphenylmethylene and 1,1-diphenylvinylidene species were postulated as intermediates in decarbonylation and deoxygenation reactions of diphenylketene;[1-3] for example, $Fe(CO)_5$ reacted with diphenylketene to yield μ-(diphenylvinylidene)-bis(tetracarbonyliron)-(*Fe–Fe*).[3] We have found that dimethylketene, which is less stable than diphenylketene, is similarly deoxygenated and decarbonylated by $Co_2(CO)_8$. Products quite different from those reported for diphenylketene are obtained, presumably through the reaction of a dicobalt-coordinated dimethylvinylidene intermediate with a second mole of $Co_2(CO)_8$.

Experimental Section

Preparation of μ_3-(Isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (1) and μ_3-(Isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (2). Dimethylketene[4] (35 g, 0.50 mol) was added to a solution of $Co_2(CO)_8$ (55 g, 0.16 mol) dissolved in 350 ml of dry, deoxygenated hexane under nitrogen. This solution was stirred for 16 hr at 25°, and a sample of the gas above the reaction was withdrawn for mass spectral analysis. Air was bubbled through the solution for 2 hr to destroy most of the unreacted $Co_2(CO)_8$. The solution was then filtered, reduced to a volume of 50 ml, and chromatographed over silica gel with hexane. The dimethylketene dimer, tetramethyl-1,3-cyclobutanedione,[5] remained on the column while the substance which appeared as a purple band was eluted. The eluate was collected, and the solvent was evaporated. The residue sublimed at 50° (10^{-3} Torr), and 4.3 g [11% yield based on $Co_2(CO)_8$] of purple crystals was collected. The nmr and mass spectral analyses showed that this product was a 1.0:1.4 mixture of μ_3-(isopropenylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) and μ_3-(isopropylmethylidyne)-*cyclo*-tris(tricarbonylcobalt)(3 *Co–Co*) (2).[6] Nmr: **1** ($CDCl_3$), δ 2.37 (d, 3, J = 1 Hz), δ 5.23 (q, 1, J = 1 Hz), δ 5.43 (broad s, 1); **2** ($CDCl_3$), δ 1.49 (d, 6, J = 6.5 Hz), δ 3.75 (septet, 1, J = 6.5 Hz). Mass spectra: **1**, parent ion at *m/e* 482; **2**, parent ion at *m/e* 484. Infrared (cyclohexane): 2040 cm^{-1} (broad terminal C=O stretch). Mass spectral analysis of the gas

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[6] Benzene reaction solvent gave a 1.0:0.28 ratio of **1**:**2**. Smaller scale reactions also gave an 11% yield of **1** and **2**.