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Reaction of Chelating Ligands with Tetracarbonylnickel, Nitrosyltricarbonylcobalt, and Dinitrosyldicarbonyliron: A Kinetics Study

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The kinetics of the interactions of several chelating ligands with $Ni(CO)_4$, $CoNO(CO)_3$, and $Fe(NO)_2(CO)_2$ are examined. In all cases, two molecules of CO are evolved, being replaced by the ligand. $Ni(CO)_4$ reacts with 1,10-phenanthroline (phen), *o*-phenylenebis(dimethylarsine) (DAS), *cis*-1,2-bis(dimethylarsino)ethylene (EDAS), and 1,2-bis(diphenylarsino)ethane (diars) in two consecutive, first-order reactions. The first is a dissociation of CO to give the intermediate $Ni(CO)_3$ which is rapidly attacked by one of the donor atoms of the chelate. The rate of this reaction is independent of the nature and concentration of the incoming ligand. The second reaction is first order but associatively activated and involves the displacement of a second CO ligand by the unattached donor atom of the chelating ligand. The rate of ring closure increases with the basicity of that atom, but steric influences may be important. For $CoNO(CO)_3$ and $Fe(NO)_2(CO)_2$, the ring closure reaction is not kinetically accessible, since the attachment of the first donor atom is rate determining. This reaction for $CoNO(CO)_3$ exhibits mixed first- and second-order kinetics (rate = $(R_1 + R_2[AA])[CoNO(CO)_3]$), the former resulting from the intervention of a solvent path to product. $Fe(NO)_2(CO)_2$ reacts with phen by a purely second-order associative path, but the arsines prove to give reactions poorly suited to kinetics analysis.

Introduction

Numerous kinetic studies have been carried out of a bidentate ligand replacing two monodentate ligands bound to a metal atom. In the majority of cases, the closing of the chelate ring was not detected kinetically.[1-18] The energetics of the second step of substitution was similar to that of the first, but the probability for ring closure was much greater than the probability of the initial step of substitution, so that the substitution step (or some earlier step on the route to product) was rate determining for the overall reaction, and the second was kinetically inaccessible. The increased probability of the reaction has been interpreted as a very high effective concentration of the unbound end of the ligand.

Some ring closures have been followed kinetically. In one case,[19] the dangling end of an ethylenediamine ligand was prevented from becoming bound to platinum(II) by protonation; the reaction proceeded when the pH was raised. Alternatively, some first steps of substitution by potential chelates render the metal center sufficiently inert to further substitution that the reaction stops, and ring closure can be observed only by raising the temperature.[20-23] Some indirect observations of ring closures have been made,[24] but the complexity of the systems has precluded calculation of the rate constant.

Ring-closure studies can in some cases be used to evaluate the effective concentration of the dangling end of the chelate by comparing the rate of the reaction to that of a second step of substitution by a similarly nucleophilic monodentate ligand. Carter and Beattie, although they observed a ring-closing rate about 1000 times faster than substitution in the absence of a chelate effect, assigned only a 30-fold enhancement factor to the high "virtual concentration".[19] Angelici,[25] on the other hand, interpreting some results of Basolo[20] on nitrosyltricarbonylcobalt, calculated an effective concentration of 500 M.

Phosphorus chelates appear to confer on the metal center of the iron and cobalt compounds too great a degree of inertness to make it convenient to study both substitution and ring closure under the same conditions. In this paper we report some studies with nitrogen and arsenic chelates (AA).

Experimental Section

Materials. Tetracarbonylnickel, $Ni(CO)_4$, was purchased from Strem Chemicals, Inc., and used without further purification. Nitrosyltricarbonylcobalt, $CoNO(CO)_3$, and dinitrosyldicarbonyliron, $Fe(NO)_2(CO)_2$, were prepared according to literature procedures[26,27] and purified by trap-to-trap distillation in a vacuum line. They were stored in foil-wrapped ampules at −78 °C prior to use. 1,10-Phenanthroline monohydrate,[28] $C_{12}H_8N_2\cdot H_2O$, was dehydrated by heating for 24 h at 80 °C under vacuum; mp 117 °C (lit.[29] mp 117 °C). *o*-Phenylenebis(dimethylarsine),[30] $C_6H_4[As(CH_3)_2]_2$, and *cis*-1,2-bis(dimethylarsino)ethylene,[31] $(CH_3)_2AsCH{=}CHAs(CH_3)_2$, were vacuum distilled prior to use. 1,2-Bis(diphenylarsino)ethane,[32] $(C_6H_5)_2AsCH_2CH_2As(C_6H_5)$, was recrystallized twice from ethanol; mp 96–99 °C (lit.[32] mp 100–101 °C). *o*-Xylene, $C_6H_4(CH_3)_2$, and decalin, $C_{10}H_{18}$, were AR grade. They were allowed to stand over 4-Å molecular sieves for several days, were distilled in a nitrogen atmosphere, and were stored with sieves under nitrogen.

Kinetics Studies. Reactions were run in all-glass vessels that included effectively constant-volume manometers. Reagent solutions were loaded in an inert-atmosphere box, thermostated in a constant-temperature bath, and then mixed. The progress of the reaction was monitored by measuring the rise in carbon monoxide pressure. Since rates were light sensitive, the reaction vessels were wrapped in foil.

Most kinetics runs were carried out under pseudo-first-order conditions with at least a sixfold excess of ligand and were followed to at least 70% completion. Final carbon monoxide pressures were used to determine the stoichiometry of the reaction. Reaction products were identified by their infrared spectra.

For reactions with iron and cobalt compounds, standard procedures were used to obtain observed first-order rate constants from the pressure data under pseudo-first-order conditions. Second-order rate constants were calculated from graphs of k_{obsd} plotted as functions of ligand concentrations. Visual line-fitting and least-squares calculations agreed. Tetracarbonylnickel exhibited kinetics indicating two consecutive, first-order reactions with comparable rate constants, k_1 and k_1', which were separated by a graphical method devised by Swain.[33]

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Table I. Average First-Order Rate Constants for Reactions 1 and 2

ligand	solvent	temp, °C	10^3k_1, s^{-1}	$10^3k_1'$, s^{-1}
phen	*o*-xylene	25	26 ± 3	16 ± 2
DAS	*o*-xylene	25	21 ± 1	7.4 ± 0.2
diars	*o*-xylene	25	24 ± 2	2.4 ± 0.3
PPh_3	*o*-xylene	25	22 ± 2	0.28 ± 0.02
EDAS	decalin	25	5.5 ± 0.3	2.6 ± 0.2
DAS	decalin	25	9.4 ± 0.1	2.1 ± 0.3
phen	*o*-xylene	0	1.3 ± 0.1	0.42 ± 0.03
DAS	*o*-xylene	0	0.85 ± 0.4	0.25 ± 0.03
DAS	decalin	0	0.16 ± 0.02	0.03 ± 0.003

Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrophotometer with a polystyrene film for reference.

Results and Discussion

Reactions with $Ni(CO)_4$. Tetracarbonylnickel was treated with *o*-phenylenebis(dimethylarsine) (DAS), *cis*-1,2-bis(dimethylarsino)ethylene (EDAS), 1,2-bis(diphenylarsino)ethane (diars), 1,10-phenanthroline (phen), triphenylphosphine (PPh_3), and *o*-phenylenebis(dimethylamine) (no reaction observed) at a variety of concentrations in *o*-xylene and decalin solvents at 0 and 25 °C. Under conditions in which the ligand was in considerable excess of the metal concentration, the reactions did not exhibit first-order kinetics. Instead, the data fit the model of two consecutive first-order reactions (eq 1 and 2) well. The change in pressure in every case indicated that

$$Ni(CO)_4 + AA \xrightarrow{k_1} Ni(CO)_3(AA) + CO \qquad (1)$$

$$Ni(CO)_3(AA) \xrightarrow{k_1'} Ni(CO)_2(AA) + CO \qquad (2)$$

two molecules of carbon monoxide were produced for each nickel. Rate constants k_1 and k_1' are given in Table I, analogous constants being shown for substitution by PPh_3 for comparison (reactions 3 and 4, $L = L' = PPh_3$).

$$Ni(CO)_4 + L \xrightarrow{k_1} Ni(CO)_3L + CO \qquad (3)$$

$$Ni(CO)_3L + L' \xrightarrow{k_1'} Ni(CO)_2LL' + CO \qquad (4)$$

Substitution reactions of tetracarbonylnickel (corresponding to reaction 3) have been extensively studied[20,24] and found to proceed by a rate-limiting dissociation of carbon monoxide, giving an intermediate, $Ni(CO)_3$, that is rapidly attacked by nucleophiles. Under a given set of conditions, the mechanism requires that k_1 not change for different ligands. Inspection of Table I shows that this condition is reasonably met. Furthermore, the rates are in accord with those measured by other workers with monodentate ligands.[35] The solvent also plays a part in the energetics; aromatic solvents associate with tetracarbonylnickel in the transition state to lower the enthalpy of activation.[20] This explains why the reaction is slower in decalin than in *o*-xylene. It may also be a clue to the difference in rates between EDAS and DAS in decalin; the latter has aromatic substituents on the arsenics, and they may stabilize the transition state or an active intermediate in the absence of aromatic solvent. We are led to the expected conclusion that the mechanism of the first step in substitution of tetracarbonylnickel by monodentate ligands is the same as that for substitution by chelating ligands, namely, a dissociative process to some degree affected by the nature of the solvent.

Table II. Carbonyl Stretching Frequencies of $Ni(CO)_2(AA)$ Compounds

AA	$\nu(CO)$	AA	$\nu(CO)$
phen	1980, 1915	diars	2005, 1940
$(PPh_3)_2$	1990, 1925	DAS	2020, 1960
EDAS	2000, 1935		

The rate constant k_1' we associate with chelate ring closure. What is observed experimentally is the evolution of a second molecule of carbon monoxide from the complex and the closed ring in the final product. Since an intermediate in which the ring is closed but carbon monoxide has not been released does not conform to the 18-electron rule[36] generally followed by such compounds, we assume that ring closure accompanies or is shortly succeeded by carbon monoxide evolution.

The ring closure (reaction 2) might be anticipated to share features in common with the second step of substitution of tetracarbonylnickel (reaction 4). Such reactions have been examined,[37] and their rates are sensitive to the identity of L but not to the concentration of L′; the mechanism therefore appears to be dissociative. The fact that the formation of $Ni(CO)_2(AA)$ from $Ni(CO)_3(AA)$ is a first-order process cannot be used, as it is in the previous reaction, to argue for a dissociative mechanism. Ring closure would appear to be an intramolecular process and therefore necessarily first order. Infrared spectra of the chelate complexes (Table II), however, argue against dissociative activation. These are the spectra of the products, but we believe that the same trends would be observed in the $Ni(CO)_3(AA)$ intermediates. The compounds are listed in order of increasing $\nu(CO)$, which can reasonably be supposed to be the order of decreasing M–C bond strength, following the usual arguments about π bonding.[38] If ring closure is dissociatively activated, this should be the order of increasing rate, since carbonyl ligands are increasingly easily displaced. Comparison of Tables I and II shows that this is not the case; phenanthroline, for example, which seems to have the strongest M–C bond, reacts most rapidly.

If the rates do not reflect the ease with which the bond to the leaving group is broken, there must be significant contribution by associative activation. The trend (nitrogen vs. arsenic nucleophiles) found here parallels that of the associatively activated substitution reactions of $CoNO(CO)_3$ and $Fe(NO)_2(CO)_2$ where pyridine is found to react faster than triphenylarsine.[39,40] Reaction rates increased with the basicity of the ligands, and this is reflected within the arsines for associative ring closure of $Ni(CO)_3(AA)$. Although the basicities of the arsines have not been measured, their relative basicities are likely to follow the same order as the analogous phosphines, with increasing aryl substitution of alkylphosphines giving weaker bases.[41] The base strength would be expected to increase in the order diars < DAS < EDAS, and the rates are also found to increase in this same order. Note that it is the basicity of the unbound donor atom of the potential chelate that dominates the reaction rate, because the effect of the bound atom is reflected in the infrared spectra and found not to correlate with the rates.

Steric features of the chelate may also contribute to the differences in the rates of ring closure. phen is a rigid molecule, and once one nitrogen is bound to nickel, the other must necessarily be in good position to attack. DAS and EDAS are rather similar to each other sterically, having more degrees of rotational freedom than phen. The dangling end of the ligand must be brought to the correct distance from the nickel, and the methyl groups must be rotated out of the way. diars has still more degrees of freedom and bulkier substituents to move out of the way. On steric grounds, the expected rates of ring closing would be phen > EDAS ≈ DAS > diars, once again in reasonable accord with the facts.

The conclusion is not as anticipated. We have argued that the evidence supports associative activation for reaction 2 but dissociative activation for the rather similar reaction 4. There must be both associative and dissociative paths to the product; at low concentrations, the dissociative path is dominant, but

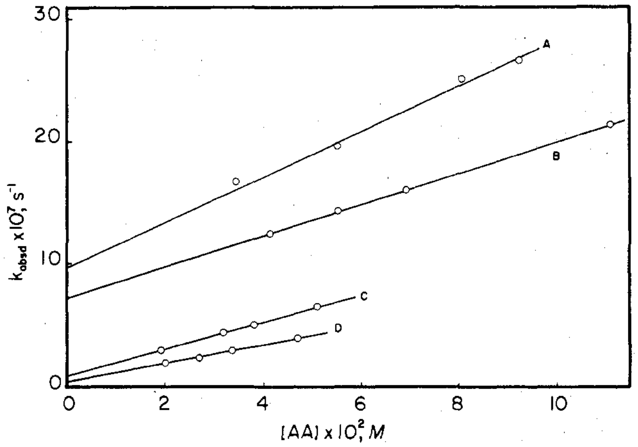

Figure 1. Observed rate constants for the reaction $CoNO(CO)_3$ + AA → $CoNO(CO)(AA)$ + 2CO as a function of ligand concentration, [AA] (T = 25° C): (A) AA = phen, $[CoNO(CO)_3] = 5.85 \times 10^{-3}$ M, *o*-xylene solvent; (B) AA = DAS, $[CoNO(CO)_3] = 6.38 \times 10^{-3}$ M, *o*-xylene solvent; (C) AA = DAS, $[CoNO(CO)_3] = 5.06 \times 10^{-3}$ M, decalin solvent; (D) AA = diars, $[CoNO(CO)_3] = 4.08 \times 10^{-3}$ M, *o*-xylene solvent.

Table III. Rate Constants for the Reaction of $CoNO(CO)_3$ with Chelating Ligands

ligand	10^7k_1, s^{-1}	10^5k_2, $M^{-1}\ s^{-1}$	ligand	10^7k_1, s^{-1}	10^5k_2, $M^{-1}\ s^{-1}$
phen[a]	9.7	18.6	diars[a]	0.30	0.78
phen[b]	4.0	7.9	DAS[c]	0.85	1.10
DAS[a]	7.2	1.28			

[a] *o*-Xylene solvent, T = 25 °C. [b] *o*-Xylene solvent, T = 30 °C. [c] Decalin solvent, T = 25 °C.

at high "virtual concentrations" of the dangling end of the potential chelate, the associative path becomes more probable. This is much like having both first- and second-order reactions: the characteristics of the first will be manifested at low concentrations and those of the second at high. Basolo[42] noted a somewhat similar situation in the reaction of $Ni(CO)_4$. Over a 100-fold increase in ligand concentration, the observed first-order rate constant increased in such a way as to suggest that about 10% of k_{obsd} was the result of a second-order term at higher concentrations. Had it been possible to carry the experiment out with a 500 M concentration of ligand as suggested by Angelici[25] for the ligand concentration, doubtless the reaction would have appeared to be second order.

Reactions with $CoNO(CO)_3$. When treated with an excess of DAS, diars, or phen, nitrosyltricarbonylcobalt produced two molecules of carbon monoxide giving good linear plots of ln (P_{CO}) vs. t (slope is k_{obsd}). This is a clear indication that the second molecule of carbon monoxide comes off in a step that is fast compared to an earlier rate-limiting step, so chelate ring closure is not observable under these conditions. Figure 1 is a graph of k_{obsd} vs. [AA]. The rate law has the form rate = $(k_1 + k_2[AA])[CoNO(CO)_3]$, and the values of the constants are listed in Table III. This form of kinetics has been reported before for substitution reactions of $CoNO(CO)_3$.[22,23,39] The value of k_2 for phen is close to that for pyridine under rather similar conditions,[39] and the values for k_1 for phen and DAS are in reasonable agreement with each other considering the errors involved in the extrapolation and with those for $AsPh_3$ and PPh_3 measured by Cardaci et al.[21,22] when a compensation is made for the difference in temperature. The large alteration in k_1 and small alteration in k_2 with the solvent change is consistent with the solvent playing an important part in the k_1 path while the ligand is the nucleophile in the k_2 path. It is very difficult to devise an explanation for the very low k_1 for diars. Perhaps, for steric reasons, diars is very ineffective in displacing a solvent molecule from the solvent-containing intermediate and will react only with an intermediate of lowered coordination number. Although other work[22,23] gives good agreement among k_1 values for different ligands at 46.4 °C, agreement is not as good at lower temperatures.

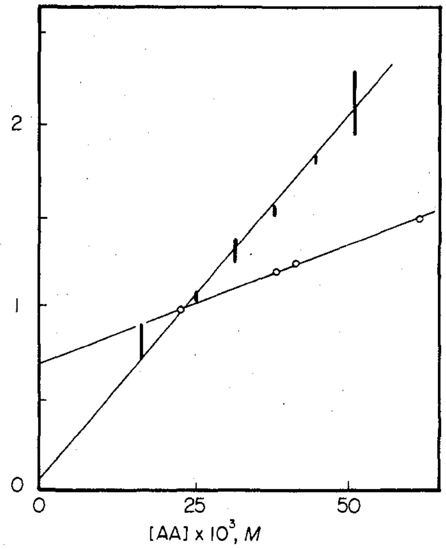

Figure 2. Observed rate constants for the reaction $Fe(NO)_2(CO)_2$ + AA → $Fe(NO)_2(AA)$ + 2CO as a function of ligand concentration, [AA] (*o*-xylene solvent, T = 25 °C): bars, AA = phen, $[Fe(NO)_2(CO)_2] = 6.50 \times 10^{-3}$ M, (error bars indicate one standard deviation on each side of the mean); ○, AA = diars, $[Fe(NO)_2(CO)_2] = 4.35 \times 10^{-3}$ M.

Reactions with $Fe(NO)_2(CO)_2$. Substitutions involving monodentate ligands with dinitrosyldicarbonyliron proceed by kinetics that are first order in complex and first order in ligand for good nucleophiles in poor donor solvents and by mixed first- and second-order kinetics (i.e., rate = $(k_1 + k_2[AA])[Fe(NO)_2(CO)_2]$) with poorer nucleophiles or in solvents that are better donors. In both cases, the mechanism is thought to be associative, the first-order term arising from rate-determining reaction with the solvent.[40,43] The compound reacted with phen (*o*-xylene solvent, T = 25 °C) producing 2 mol of carbon monoxide by a second-order process (see Figure 2), $k_2 = 4.0 \times 10^{-3}\ M^{-1}\ s^{-1}$. The line in Figure 2 shows the calculated best fit of the data. Although there is a small positive intercept, it is no bigger than the average standard deviation of the points. Under similar conditions,[40] the value for monosubstitution by pyridine is $5.6 \times 10^{-3}\ M^{-1}\ s^{-1}$. The data are consistent with a mechanism in which there is rate-determining, associative attack of the metal by phen, followed by rapid ring closure.

Results for two chelating arsines, diars and DAS (same conditions), must be viewed with some doubt. diars gave data fitting a conventional two-term rate law (see Figure 2), $k_1 = 6.9 \times 10^{-5}\ s^{-1}$ and $k_2 = 1.31 \times 10^{-3}\ M^{-1}\ s^{-1}$. However under similar conditions,[43] $AsPh_3$ gave $k_1 = 0$ and $k_2 = 1.5 \times 10^{-5}\ M^{-1}\ s^{-1}$. DAS gave poor reproducibility (but good kinetics plots) under pseudo-first-order conditions, but kinetics runs with equal concentrations of reactants fit P_{CO}^{-1} vs. t plots well, a crucial test of second-order processes, since with mixed rate laws the first-order term dominates the rate. The reaction was then assumed to have no first-order term in its rate law. Data from individual reactions that were run under pseudo-first-order conditions could then be used to calculate the second-order rate constant, the averaging being $(1.0 \pm 0.6) \times 10^{-3}\ M^{-1}\ s^{-1}$, again a doubtful value.

Registry No. $Ni(CO)_4$, 13463-39-3; $CoNO(CO)_3$, 14096-82-3; $Fe(NO)_2(CO)_2$, 13682-74-1; DAS, 13246-32-7; EDAS, 13787-53-6; diars, 4431-24-7; phen, 66-71-7; PPh_3, 603-35-0; $Ni(CO)_2(phen)$, 36454-23-6; $Ni(CO)_2(PPh_3)_2$, 13007-90-4; $Ni(CO)_2(EDAS)$, 32354-82-8; Ni(CO)$_2$(diars), 69204-58-6; Ni(CO)$_2$(DAS), 32355-21-8.

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Electron-Transfer Reactions of Copper(III)–Peptide Complexes with Hexachloroiridate(III)

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Oxidation–reduction reactions involving the peptide complexes of copper(III) and copper(II) provide the first opportunity to determine the speed of electron-transfer reactions between these oxidation states as well as providing an example of electron transfer between two predominantly square-planar complexes. Although the reactions between $IrCl_6^{3-}$ and copper(III)–peptides are uphill electron transfers, the reactions can be forced in this direction by taking advantage of the relatively rapid reaction of acids with the copper(II)–peptides compared to the analogous reactions of the copper(III)–peptides. Application of Marcus' theory for outer-sphere electron transfer to the neutral copper(III)–peptides permits calculation of an apparent self-exchange rate constant for the copper(III)–copper(II) species as 7×10^7 M^{-1} s^{-1} (25.0 °C, 0.1 M ionic strength). An alternative mechanism with electron transfer via a chloride bridge between iridium and copper also is possible.

Introduction

Copper(III)–deprotonated-peptide complexes are readily prepared by chemical or electrochemical oxidation and are moderately stable in aqueous media.[1-4] The copper(III)–peptides have intense charge-transfer bands in the vicinity of 250 and 365 nm. The complexes have no ESR spectra, and they are very slow to undergo ligand substitution reactions. Their properties are characteristic of low-spin, d^8, square-planar complexes. Although crystal structures of the copper(III)–peptide complexes have not been obtained, the crystal structure of the triply deprotonated tetraglycine complex of copper(II), $Cu^{II}(H_{-3}G_4)^{2-}$, has been determined.[5] This d^9 complex has four nitrogens coordinated to copper in a nearly square-planar arrangement with Cu–N distances of 2.03 Å (for the amine) and 1.91–1.94 Å (for the deprotonated peptides). The crystal structure of a related complex, *o*-phenylenebis(biuretato)cuprate(III), has been determined.[6] The copper atom is surrounded by an approximately planar arrangement of four nitrogen atoms with short Cu–N distances (1.82–1.89 Å).

Oxidation–reduction reactions involving the peptide complexes of copper(II) and copper(III) provide the first opportunity to determine the speed of electron-transfer reactions between these oxidation states as well as providing an example of electron transfer between two predominantly square-planar complexes. The $Ir^{IV}Cl_6^{2-}$–$Ir^{III}Cl_6^{3-}$ redox couple was chosen to study the electron-transfer characteristics of the $Cu^{III,II}$ systems because the iridium complexes are known to undergo outer-sphere electron-transfer reactions with a variety of compounds[7] and because the self-exchange rate constant has been evaluated.[8] Both of these iridium complexes have very slow substitution reactions.[9] Copper(III)–peptides are formed by $IrCl_6^{2-}$ oxidation of the corresponding copper(II) complexes,[1,2] but the reactions are too fast to measure by stopped-flow techniques.[10,11] This difficulty has been circumvented by measuring the rates of the reverse reactions between $IrCl_6^{3-}$

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