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Kinetics and Mechanism of Substitution of the Quadruply Bonded Molybdenum(II) Aqua Dimer with Thiocyanate and Oxalate

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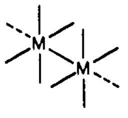
Equilibration kinetics, rate law $k_{eq} = k_1[Mo_2^{4+}] + k_{-1}$, are observed for the reaction of Mo_2^{4+} (10-fold excess) with thiocyanate in aqueous trifluoromethanesulfonic acid (HTFMS) solution, $I = 0.10$ M (NaTFMS). Rate constants at 25 °C are $k_1 = 590\ M^{-1}\ s^{-1}$ for the forward reaction and $k_{-1} = 0.21\ s^{-1}$ for the reverse. Activation parameters for k_1 are $\Delta H_1^* = 12.8$ kcal mol^{-1} and $\Delta S_1^* = 0.72$ cal K^{-1} mol^{-1}. A more complex rate law is observed for the reaction with oxalate: $k_{eq} = k_2K[Mo_2^{4+}]/(K + [H^+]) + k_{-2}$, where K is the acid dissociation constant for $H_2C_2O_4$, consistent with $HC_2O_4^-$ being the principal reactant. The $[H^+]$ dependence was tested for at $I = 0.20$ (NaTFMS) to allow a variation in $[H^+]$ from 0.050 to 0.192 M. A spectrophotometric method was used to determine the pK for $H_2C_2O_4$ of 1.20 (independent of temperature 10–40 °C). Rate constants at 25 °C, $I = 0.10$ M (NaTFMS), are $k_2 = 43\ M^{-1}\ s^{-1}$ and $k_{-2} = 4.7 \times 10^{-3}\ s^{-1}$ with $\Delta H_2^* = 12.4$ kcal mol^{-1} and $\Delta S_2^* = -23.2$ cal K^{-1} mol^{-1}. Whereas NCS^- is monodentate, oxalate as $HC_2O_4^-$ bridges the Mo_2^{4+} unit (with retention of the proton), and an extra step is therefore involved in the substitution process.

Introduction

Molybdenum in oxidation state II forms dimeric diamagnetic compounds, of which $[Mo_2(O_2CCH_3)_4]$ and $[Mo_2Cl_8]^{4-}$ are examples, having short metal–metal bonds of around 2.1 Å.[1-3] Eclipsed structures are consistent with δ-bond formation and quadruple metal–metal bonding.[1] The Mo(II) aqua dimer $Mo_2(H_2O)_8^{4+}$, first prepared by Bowen and Taube,[4] also has a quadruply bonded structure (see structure **1**).



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Three dimeric aqua ions are now known in which metal–metal bonds (no bridging ligands) are responsible for the binuclear structure. These are the mercury(I) dimer, Hg_2^{2+}, which has a dominant linear diaqua structure $H_2O–Hg–Hg–H_2O$,[5] and the rhodium(II)[6] and molybdenum(II) octaaqua ions. Complexes of Rh^{II}_2 and Mo^{II}_2 exhibit weak additional bonding to axial ligands,[2] and both aqua ions can accordingly be represented more fully as $[Mo_2(H_2O)_8(H_2O)_2]^{4+}$.

Little attention has been paid to the reactions of such dimers in solution. Thus at a time when substitution reactions of most aqua ions are fairly well understood,[7] there are no studies as to rates or mechanisms of substitution of these ions. The kinetics of the 1:1 reactions of Mo_2^{4+} with thiocyanate and oxalate are reported in this paper.

Experimental Section

Preparation of Mo_2^{4+}. Commercially available molybdenum hexacarbonyl (Koch-Light) was used as starting material. Four stages were involved in the preparation. Tetrakis(μ-acetato)dimolybdenum(II), $[Mo_2(O_2CCH_3)_4]$, was obtained in the first stage by a procedure already described.[8] The yellow crystals obtained were used for the second stage without further purification. To convert to the octachlorodimolybdate(II), $K_4[Mo_2Cl_8]\cdot 2H_2O$,[9] a solution of concentrated HCl (130 mL) at 0 °C was first saturated with HCl gas for 7 min, potassium chloride (3.6 g) was added with stirring, and the mixture was warmed to room temperature. To this solution was added $[Mo_2(O_2CCH_3)_4]$ (2.6 g) and the mixture stirred for a further 1 h. The purple-red solid was filtered off, washed with absolute ethanol (20 mL), and dried first under a stream of N_2 and then over KOH in a vacuum desiccator for 6 h. The third stage was carried out under O_2-free conditions. A solution of $K_4[Mo_2Cl_8]\cdot 2H_2O$ (3.3 g; 85% yield) was stirred in O_2-free 0.1 M H_2SO_4 (300 mL) for 3 h. Potassium sulfate (15 g) was added in a glovebag under N_2, and the mixture was stirred for a further 10 min. Pink $K_4[Mo_2(SO_4)_4]\cdot 3.5H_2O$ (3.6 g; 95% yield) was filtered off,[10] washed with alcohol and ether, dried over silica gel, and stored at 0–4 °C under N_2. Rigorous air-free conditions were adopted for the final stage[4] in which $[Mo_2(SO_4)_4]^{4-}$ (as required) was dissolved in O_2-free ca. 0.1 M trifluoromethanesulfonic acid (HTFMS) in a ca. 100-mL capacity centrifuge tube, and barium trifluoromethanesulfonate, obtained by addition of $Ba(OH)_2$ (BDH, Analar) to the acid (Ba^{2+} in <20% excess of the sulfate), was then added. The total volume was around 50 mL. To aid precipitation/coagulation of the $BaSO_4$, the solution was carefully heated to 40 °C for 5 min and then cooled in ice to 0 °C. As a precaution, N_2 was passed through the tube via entry and exit syringe needles during this procedure. Following centrifugation, the supernatant pink solution was transferred by using Teflon tubing and N_2 gas pressure. Stoichiometric amounts of Ba^{2+} can be used with more time and/or care for precipitation.

Solutions with the Mo_2^{4+} absorbance peak at 510 nm ($\epsilon = 370\ M^{-1}\ cm^{-1}$) and a minimum at 420 nm ($\epsilon = 120\ M^{-1}\ cm^{-1}$) (both ε's per dimer) could be kept under N_2 for up to 3 h. Pure samples do not have a peak at 370 nm. The band at 510 nm, assigned to a $\delta \rightarrow \delta^*$ transition,[11] is common to other Mo(II) dimers (Figure 1). The Mo(II) was determined by addition of a 100-fold excess of Fe(III) to convert Mo(II) to Mo(VI) (20 min) and titration of the Fe(II) with Ce(IV). Stock solutions of Mo_2^{4+} of concentration $(1–6) \times 10^{-3}$ M, in HTFMS of concentration 0.05–0.20 M, were prepared as required.

Other Reactants. Colorless trifluoromethanesulfonic acid (Aldrich) was obtained from the commercial liquid by distillation under reduced pressure (the acid decomposes at the normal boiling point) from the side arm at a water tap. A substantial middle fraction was retained. Sodium thiocyanate (BDH, technical grade) was recrystallized twice from ethanol and dried under vacuum for ca. 12 h. Oxalic acid or sodium oxalate (BDH, Analar) was used. Sodium trifluoromethanesulfonate (NaTFMS) was prepared by slow neutralization of HTFMS (~4 M) with concentrated NaOH (BDH Analar) at ~0 °C.

Acid Dissociation Constant of Oxalic Acid. A UV range spectrophotometric method as described by Albert and Serjeant[12] was used to determine the acid dissociation constant, K, for (1). From the

$$H_2C_2O_4 \overset{K}{\rightleftharpoons} H^+ + HC_2O_4^- \qquad (1)$$

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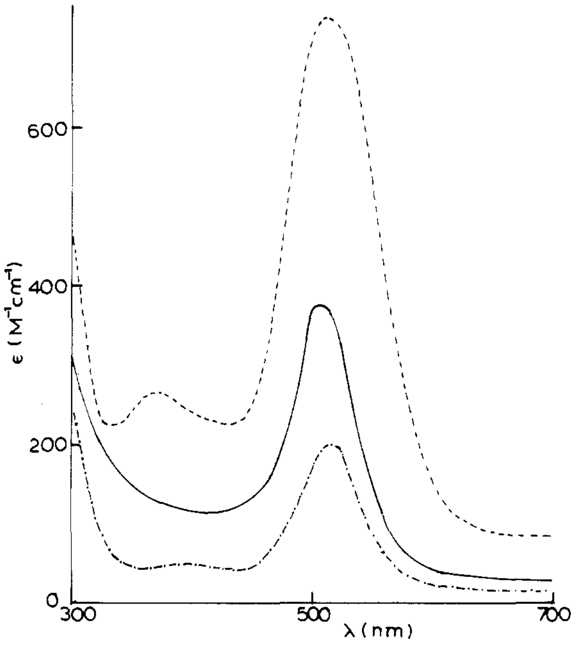

Figure 1. UV-visible spectra of the Mo_2^{4+} ion: aqua ion in 0.1 M HTFMS (—); $[Mo_2Cl_8]^{4-}$ in 2 M HCl (- - -); $[Mo_2(SO_4)_4]^{4-}$ in 2 M H_2SO_4 (···). The same $\delta \rightarrow \delta^*$ transition is observed in all three cases.

different absorbances of $H_2C_2O_4$ and $HC_2O_4^-$ at 205 nm (Perkin-Elmer Lambda 5), a value of K was obtained. The $[H^+]$ range (0.06–0.15 M) adjusted by addition of HCl was such that further acid dissociation of $HC_2O_4^-$ ($pK = 3.67$)[13] was not relevant. The ionic strength was adjusted to 0.20 M with NaTFMS. Values of the pK obtained from an average of three measurements at different $[H^+]$ values are 1.19 ± 0.06 (10 °C), 1.21 ± 0.07 (25 °C), and 1.21 ± 0.07 (40 °C), in satisfactory agreement with previous determinations.[13-15] No significant variation in K with ionic strength 0.10–0.20 M is apparent. A value of 1.20 (independent of temperature) has been assumed in all subsequent calculations in this paper.

Kinetic Studies. A Dionex 110 stopped-flow spectrophotometer was used to monitor the reaction with thiocyanate, and a Perkin-Elmer 550 for the oxalate (conventional time range) study. Ionic strengths were adjusted to $I = 0.10$ M (NaTFMS) except for the study of the $[H^+]$ dependence of the oxalate reactions when a higher value of $I = 0.20$ M (NaTFMS) was adopted. A comparison of pK values for (1) at $I = 0.20$ M with literature values at other ionic strengths indicated that no marked dependence is to be expected over the range 0.10–0.20 M, and variations are unlikely to be outside the experimental errors for the determinations reported here. Solutions of Mo_2^{4+} for the NCS^- study were prepared with the addition of a 25% excess of Ba^{2+}, where such an excess was shown to have no effect on rate constants. In the oxalate study, no excess of Ba^{2+} could be tolerated, since rate constants were found to vary from 1.39×10^{-2} s^{-1} (40% excess) to 1.89×10^{-2} s^{-1} (20% excess) to 2.70×10^{-2} s^{-1} (no excess).

Conditions for kinetic runs were with the Mo_2^{4+} reactant in ca. 10-fold excess. The same rate constants were obtained with Mo_2^{4+} in 30-fold excess. First-order rate constants k_{eq}, with Mo_2^{4+} in 30-fold excess, were obtained from the slope of plots of absorbance (A) changes ln ($A_\infty - A$) against time, where A_∞ was the final observed absorbance.

Treatment of Data. A nonlinear least-squares program ($1/k^2$ weighting) was used in the evaluation of activation parameters.

Results

Reaction with NCS^-. Formation of the 1:1 complex (eq 2)

$$Mo_2^{4+} + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo_2NCS^{3+} \qquad (2)$$

was monitored at 550 nm. Equilibration rate constants, k_{eq} (Table I),[16] gave a linear dependence on $[Mo_2^{4+}]$ (Figure 2), consistent with (3). Rate constants k_1 and k_{-1} and activation parameters are listed in Table IV.

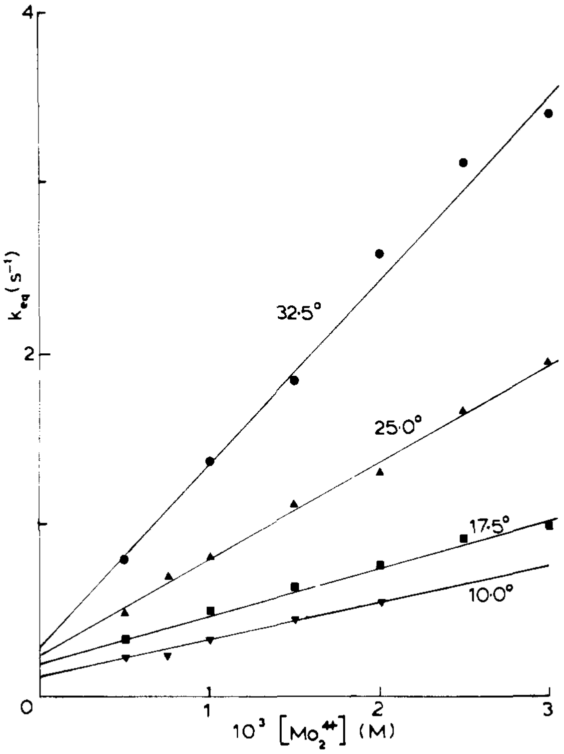

Figure 2. Dependence of equilibration rate constants, k_{eq}, on $[Mo_2^{4+}]$ for the 1:1 reaction of NCS^- with Mo_2^{4+}, the latter in large 10-fold excess ($I = 0.10$ M (NaTFMS)).

Table IV. Summary of Rate Constants (25 °C) and Activation Parameters $\Delta H^\ddagger$ (kcal mol^{-1}) and $\Delta S^\ddagger$ (cal K^{-1} mol^{-1}) for the Reaction of Mo_2^{4+} with NCS^-, k_{-1} (M^{-1} s^{-1}) and k_{-1} (s^{-1}) As Defined in (2), and $HC_2O_4^-$, k_2 (M^{-1} s^{-1}) and k_{-2} (s^{-1}) As Defined in (4) ($I = 0.10$ M (NaTFMS))

Reaction of Mo_2^{4+} with NCS^-	
$k_1 = 590 \pm 23$	$k_{-1} = 0.21 \pm 0.04$
$\Delta H_1^\ddagger = 13.8 \pm 0.8$	$\Delta H_{-1}^\ddagger = 3.9 \pm 1.8$
$\Delta S_1^\ddagger = 0.7 \pm 2.6$	$\Delta S_{-1}^\ddagger = -48.6 \pm 6.4$
Reaction of Mo_2^{4+} with $HC_2O_4^-$	
$k_2 = 43 \pm 1.2$	$k_{-2} = (4.7 \pm 0.6) \times 10^{-3}$
$\Delta H_2^\ddagger = 12.4 \pm 0.1$	$\Delta H_{-2}^\ddagger = 13.7 \pm 2.7$
$\Delta S_2^\ddagger = -23.3 \pm 2.6$	$\Delta S_{-2}^\ddagger = -23.1 \pm 9.2$

$$k_{eq} = k_1[Mo_2^{4+}] + k_{-1} \qquad (3)$$

Reaction with Oxalate. This reaction was monitored at 590 nm, at which wavelength the largest absorbance increase was observed. For the range of $[H^+]$ studied, 0.050–0.192 M, oxalate is present as $H_2C_2O_4$ and $HC_2O_4^-$ in rapid equilibrium (eq 1). No evidence was obtained for participation of $C_2O_4^{2-}$, which is at a low level ($<2 \times 10^{-9}$ M) for the conditions investigated. With the assumption that $HC_2O_4^-$ is reactive, the equilibrium can be expressed as in (4). The rate law

$$Mo_2^{4+} + HC_2O_4^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Mo_2C_2O_4H^{3+} \qquad (4)$$

dependence (5), derived from (1) and (4), was found to apply.

$$k_{eq} = \frac{k_2K[Mo_2^{4+}]}{K + [H^+]} + k_{-2} \qquad (5)$$

Thus at constant $[Mo_2^{4+}]$, rate constants k_{eq} (Table II)[16] gave a linear dependence on $K/(K + [H^+])$ (Figure 3). With $[H^+]$

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[16] Supplementary material: see paragraph at end of paper.

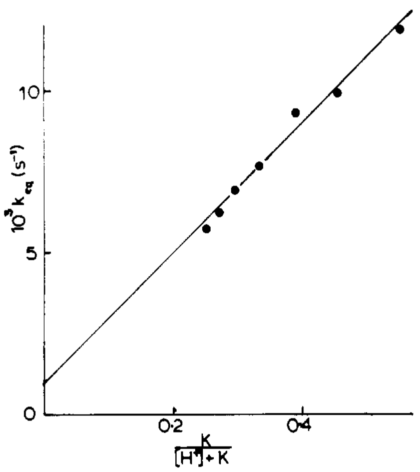


Figure 3. Dependence of equilibration rate constants, k_{eq}, for the 1:1 complexing of oxalate (5.0×10^{-5} M) with Mo_2^{4+} (5.0×10^{-4} M) on [H^+] at 20 °C (I = 0.20 M (NaTFMS)). A value of K, as defined in (1), of 0.063 M has been used.

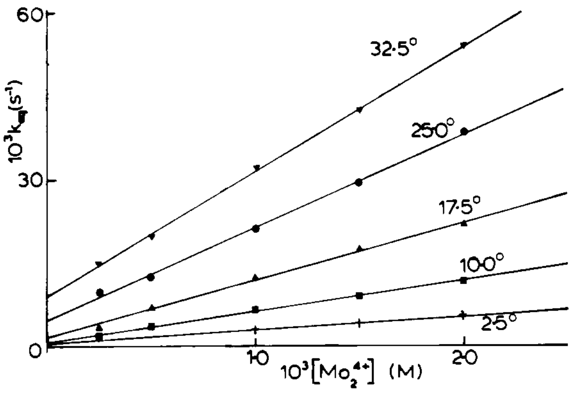
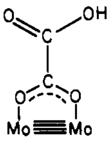


Figure 4. Dependence of equilibration rate constants, k_{eq}, for the 1:1 complexing of oxalate with Mo_2^{4+} on [Mo_2^{4+}] (reactant present in large excess; [H^+] = 0.10 M; I = 0.10 M (HTFMS)).

constant the variation of k_{eq} with [Mo_2^{4+}] was investigated (Table III)[16] and a linear dependence observed (Figure 4). From the temperature dependence activation, parameters for k_2 and k_{-2} were obtained. Within experimental error no contributions from $H_2C_2O_4$ (or $C_2O_4^{2-}$) were evident.

Discussion

Structural studies on two $(NH_4)_4[Mo_2(NCS)_8]$ hydrates have demonstrated that thiocyanate is monodentate and N-bonded to the molybdenum.[17] No evidence has been reported, suggesting that thiocyanate (or halide) bridging of two molybdenums is possible in Mo^{II}_2. Also, from structural studies on a range of complexes such as $[Mo_2(O_2CCH_3)_4]$, it is clear that μ-carboxylato bridges readily form and that monodentate carboxylate coordination is not observed.[1,3] Therefore, with oxalate, bridging of the two Mo's is assumed. Of the two types of bridging, evidence in support of A rather than B has been obtained. Thus, an orange-red solid prepared by addition of excess oxalate to Mo_2^{4+} at pH 1 gives an infrared band at 1740 cm^{-1}, consistent with protonation of free carboxylate as indicated in A.[18,19] That oxalate in B does not readily protonate has been amply demonstrated by consideration of complexes such as $[Co(NH_3)_4(C_2O_4)]^+$ containing oxalate as a five-membered chelate ring.[20] Furthermore, the kinetic form of the rate law clearly indicates that $HC_2O_4^-$ is the reactant and, since k_{-2} is independent of [H^+], that A and not B is relevant. The rate constant k_2 is 1 order of magnitude smaller than that observed for NCS^- (Table IV). Since, with oxalate, only a single kinetic step first order in oxalate is observed, monodentate complex formation is the rate-determining step, followed by rapid bridge formation, or the first step is a relatively rapid equilibrium prior to bridge formation. It is difficult to choose between these two possibilities at present. If k_2 = 43 M^{-1} s^{-1} for monodentate complexing of HC_2O_4 to Mo_2^{4+}, then clearly (in view of the rate constant 590 M^{-1} s^{-1} for NCS^-) there is a significant dependence of rate constants for this step on the identity of the 1− anion.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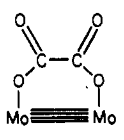
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Table V. Comparison of Kinetic Parameters for the 1:1 Reactions of Aquametal Ions with NCS^-

metal ion	$10^{-3}k$(25 °C), M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
Mo_2^{4+}	0.59	13.8	0.7
VO^{2+} [a]	11.5	10.8	−3.7
TiO^{2+} [b]	6.1	11.7	−4.0

[a] Reference 21. [b] Reference 22.

Activation parameters for the reaction of NCS^- with Mo_2^{4+} are compared with those obtained for the complexing of NCS^- to VO^{2+} and TiO^{2+} in Table V.[21,22] Saito and Sasaki[7] have summarized the situation for VO^{2+} and TiO^{2+} in their recent review. Thus rapid (essentially diffusion-controlled) equilibration of NCS^- in the labile axial position (K_a) is followed by a subsequent slower step (k_b) leading to NCS^- occupancy of the basal plane of the complex. Clearly a similar mechanism is possible for Mo_2^{4+}, since confinement of electron density to the Mo–Mo locality makes the situation directly comparable to that of the oxo anions VO^{2+} and TiO^{2+} (see structures C and D). Low d-electron populations are an additional feature that the systems have in common. Accordingly, k_1 for the Mo_2^{4+} reaction corresponds to the product $K_a k_b$. Saito and colleagues[23] have also studied the trifluoroacetate ligand exchange on $[Mo_2(O_2CCF_3)_4]$ in acetonitrile by ^{19}F NMR spectroscopy and arrived at the same conclusion with regard to mechanism.


(Mo^{II} dimer)
C


(M = V^{IV}, Ti^{IV})
D

Crystallographic studies have indicated that the Mo–Mo distance remains fairly invariant at 2.1 Å for a wide range of monodentate and bridging ligands.[1-3] The considerably larger $\Delta H^{\ddagger}$ value for dissociation of the oxalato complex (13.7 kcal mol^{-1}) as compared for that for NCS^- (3.9 kcal mol^{-1}) is consistent with high kinetic stability of the μ-carboxylato product.

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Whether the type of behavior observed here will hold for the Rh$_2^{4+}$ and Hg$_2^{2+}$ aqua ions is of further interest. With Rh$^{II}_2$ the higher d-electron population and with Hg$^{I}_2$ the linear diaqua structure are features that could well lead to different behavior.

Acknowledgment. We are grateful to the Swiss Science Foundation for a fellowship (to P.L.) and to Carleton College, Northfield, MN, for a leave of absence (to J.E.F.).

Registry No. Mo$_2^{4+}$, 86711-98-0; NCS$^-$, 302-04-5; HC$_2$O$_4^-$, 920-52-5.

Supplementary Material Available: Listings of rate constants (Tables I-III) (3 pages). Ordering information is given on any current masthead page.

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Oxygen Atom Transfer Reactions. 4. Nitro/Nitrito Exchange in the Reaction of Nickel Dinitro Complexes with CO

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The oxidation of CO by Ni(NO$_2$)$_2$L$_2$ complexes produces CO$_2$ and Ni(NO$_2$)(NO)L$_2$ quantitatively. Reaction with C^{18}O (99.6%) shows that the primary oxidation product is C^{16}O^{18}O and that no ^{18}O is incorporated into the nickel complexes. In several cases (L = P(CH$_3$)$_2$(C$_6$H$_5$), P(C$_6$H$_{11}$)$_3$, and P(C$_4$H$_9$)$_3$), carbonyl intermediates were directly observed by using infrared and ^{31}P{^{1}H} NMR spectroscopy. Thus, these reactions are associative, forming Ni(CO)(NO$_2$)$_2$L$_2$ followed by an intramolecular transfer of an oxygen atom to CO and terminated by loss of CO$_2$. The solution stereochemistries of the reactants, intermediates, and products have also been investigated in the temperature range 190–330 K. The NO$_2$-containing complexes exhibited temperature-dependent ^{31}P{^{1}H} NMR signals indicative of exchange between –NO$_2$ and –ONO isomers, but no exchange between –NO and –NO$_2$ ligands was observed. Determination of the identity and solution stereochemistry of these species using ^{31}P{^{1}H} NMR spectra was aided by ^{15}N substitution (95%).

Introduction

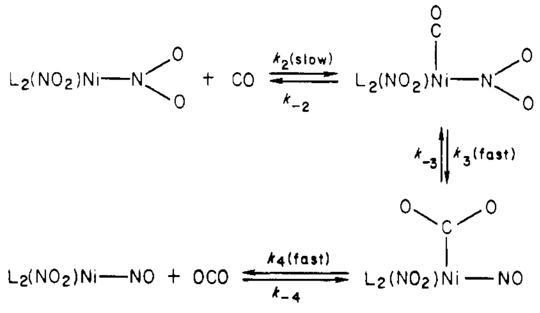
The oxidation of CO by Ni(NO$_2$)$_2$L$_2$ complexes of tertiary phosphines is well-known and has been reported previously:[1]

$$\mathrm{Ni(NO_2)_2L_2 + CO \rightarrow Ni(NO_2)(NO)L_2 + CO_2} \quad (1)$$

The observed rate law for the reaction of CO with Ni(NO$_2$)$_2$dppe and Ni(NO$_2$)$_2$(PMe$_3$)$_2$ is first order each in CO and nickel complex (k_2 values[1b,c] are 2.1 × 10^{-1} and 6.0 × 10^{-1} L mol^{-1} s^{-1}, respectively) and typical of square-planar complexes of nickel(II).[2] These observations are consistent with the previously proposed mechanism[1b–e] (Scheme I) in which the rate-determining step is formation of the monocarbonyl complex Ni(CO)(NO$_2$)$_2$L$_2$, followed by transfer of an oxygen atom to CO and terminated by loss of CO$_2$.

The only prior information about reactions 3 and 4 (Scheme I) was derived from the ^{18}O-labeling studies of Doughty et al.[1c] in which the observed distribution of ^{18}O in product CO$_2$ suggested that the nickel carbon dioxide complexes are sufficiently long-lived to undergo oxygen exchange with the NO$_x$ ligands (reaction 3) before irreversibly losing CO$_2$ (reaction 4). The recent observation[1d] of equilibria between –NO$_2$ and –ONO in these complexes also calls into question which isomer is responsible for oxygen atom transfer to CO. Moreover, direct attack of CO on the coordinated NO$_2$ ligand has recently been indicated for cobalt complexes[3] and has not been completely ruled out for the nickel complexes by the results of experiments thus far reported. It is the purpose of the present investigation to further elucidate the mechanism(s) of reaction 1 by examining the solution stereochemistries of reactants, products, and observable intermediates.

Scheme I. Proposed Mechanism for Oxidation of CO by -NO$_2$



Experimental Section

All operations were carried out under dry nitrogen unless otherwise specified. Solvents were of reagent grade and were purified by distillation immediately prior to use according to published procedure.[4] Na^{15}NO$_2$ (95% enriched) and C^{18}O (99.63% enriched) were purchased from Prochem. Microanalyses were carried out by Huffman Laboratories, Wheatridge, CO, and Atlantic Microlabs, Atlanta, GA. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer Model 387 spectrometer. Electronic spectra were recorded on a Cary 14 UV-visible spectrophotometer.

Materials. Ni(NO$_2$)$_2$L$_2$ (L = PMe$_3$, PEt$_3$, PMe$_2$Ph, PPh$_3$, P-*n*-Bu$_3$, PCy$_3$, $^1/_2$ dppe, $^1/_2$ *cis*-vdpp, and $^1/_2$ dppp[5] were prepared by adding

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(5) Me, Et, and Ph have their usual meaning, *n*-Bu is *n*-butyl, Cy is cyclohexyl, dppe is 1,2-bis(diphenylphosphino)ethane, *cis*-vdpp is *cis*-1,2-bis(diphenylphosphino)ethene, and dppp is 1,3-bis(diphenylphosphino)propane.