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Oxygen Isotopic Effect on the Reduction of Aquo- and Hydroxopentaamminecobalt(III)

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The oxygen isotopic fractionation factor (d ln O^{16}/d ln O^{18} = f) in the reduction of $(NH_3)_5CoOH_2^{3+}$ by the "outer-sphere" reagent $Ru(NH_3)_6^{2+}$ is observed to be 1.021 and in the reduction of $(NH_3)_5CoOH^{2+}$ is 1.017. The latter result differs quite markedly from that observed (f = 1.04) in the reaction of the hydroxy ion with Cr^{2+}, and it thus seems likely that the value of f may be useful in classifying the reaction mechanism. The reducing agents V^{2+} and Eu^{2+} and a number of metals acting as cathodes show values of f close to those observed for $Ru(NH_3)_6^{2+}$, indicating that the activation of the Co(III) complex demanded by them is similar. Several reducing agents complexed by EDTA give values of f close to unity, and it is suggested that in these cases inner-sphere mechanisms operate with substitution in the reducing agent being rate determining.

Introduction

The experiments which have been done on oxygen[1] and nitrogen[2] fractionation effects in the reaction of $(NH_3)_5CoOH_2^{3+}$ with Cr^{2+} suggest that this kind of measurement can be useful in characterizing the activated complex for an oxidation–reduction reaction of metal complexes. The reaction referred to above proceeds by way of an inner-sphere activated complex, and the oxygen isotopic fractionation factor is quite large (d ln O^{16}/d ln O^{18} = f = 1.035 for the reaction of the hydroxo complex). The large value of f is consistent with the view that stretching the Co–O bond is important in the activation leading to electron transfer.

Having before us an example of the magnitude of f for a reaction involving the inner-sphere activated complex, we undertook to measure f also for the reaction with $(NH_3)_5CoOH_2^{3+}$ of the reducing agent $Ru(NH_3)_6^{2+}$, which because of the inertia to substitution of the coordinated ammonias[3] is constrained to react by a mechanism involving an outer-sphere activated complex. If the activation process is different for the two kinds of processes, it is reasonable to expect this difference to be reflected in the values of f. The value of f for the reaction of $Ru(NH_3)_6^{2+}$ with $(NH_3)_5CoOH_2^{2+}$ indeed proved to be markedly different from that for the corresponding reaction with Cr^{2+} as the reducing agent. Accordingly, it seemed worthwhile to extend the measurements to reducing agents which react with the aquo ion by unknown mechanisms. This paper is a report on the results of our measurements of f for $Ru(NH_3)_6^{2+}$, V^{2+}, Eu^{2+}, Cu^+, some EDTA complexes, and some electrodes acting as reducing agents on $(NH_3)_5CoOH_2^{3+}$.

Experimental Section

Materials.—$[(NH_3)_5CoOH_2](ClO_4)_3$ was prepared by acidifying carbonatopentaamminecobalt(III) nitrate[4] with 2 M $HClO_4$.[5] Part of the complex was enriched in O^{18} by equilibration with O^{18}-enriched water. $[(NH_3)_5CoOH_2]Cl_3$ was prepared by adding KCl to a solution of aquo perchlorate, thus removing most of the perchlorate ion; cold concentrated HCl was then added to precipitate the chloride.

A solution containing Cr^{2+} was prepared following standard procedure using amalgamated zinc as the reducing agent. Chromous ion was used to reduce $Ru(NH_3)_6^{3+}$ to $Ru(NH_3)_6^{2+}$, the oxidizing agent being in slight excess. The source of $Ru(NH_3)_6^{3+}$ was $Ru(NH_3)_6Cl_3$ supplied by Johnson Matthey, London. The reducing agents, V^{2+} and Eu^{2+}, were obtained by electrolytic reduction of NH_4VO_3 and Eu_2O_3 in $HClO_4$(aq). A solution containing $Cu(NH_3)_2^+$ was made up by dissolving CuCl in dilute NH_3(aq). The CuCl was purified by dissolving it in concentrated HCl, then diluting the solution to precipitate CuCl, whereupon the solid was collected and washed with water. All operations were performed using a blanket of N_2 gas to exclude O_2. The EDTA complexes of Cr^{2+}, Fe^{2+}, and Eu^{2+} were prepared by adding solutions containing the ions of EDTA in NH_3(aq), using a 10 to 20% excess of EDTA.

Reduction Procedure.—The reactions were carried out by adding the reducing solution to 2.5 × 10^2 ml of solution containing *ca.* 10 g of the Co(III) salt and other reagents as necessary. Enough reducing agent was added to result in the reduction of about three-fourths of the Co(III). The solutions were stirred vigorously during the reduction process. For the reactions in acidic solution, enough acid was present to account for all of the NH_3 released and leaving *ca.* 20% in excess. Whenever possible, $HClO_4$ was used. When $Ru(NH_3)_6^{2+}$ was the reducing agent, HCl rather than $HClO_4$ was the acid. To make our results with Cr^{2+} comparable to the earlier results, 0.2 M H_2SO_4 was used as the reaction medium in this case.

For the reactions in alkaline media, the solution was *ca.* 0.8 M in NH_3. With $Cu(NH_3)_2^+$ as reducing agent, the aquo chloride rather than perchlorate was used as the source of the aquo ion, to avoid the precipitation of $[Cu(NH_3)_2]ClO_4$. For the electrolytic reduction, the cathodes were pretreated by dipping into concentrated HNO_3 for 30 sec and then rinsed with distilled water. After reduction, the excess $(NH_3)_5CoOH_2^{3+}$ was precipitated as the bromide by adding to the solution an equal volume of ice-cold concentrated HBr. The precipitate was filtered after standing at 0° for ~2 hr, washed with HBr(aq) (1 mole to 3 moles of H_2O), and dried. When $Ru(NH_3)_6^{2+}$ is the reducing agent, the precipitate contains also $Ru(NH_3)_6Br_3$. The two compounds were separated by fractional dissolution in water and fractional precipitation with $HClO_4$ and HBr. The purity of the isolated Co(III) complex was checked spectrophotometrically.

The extent of reduction was determined by analysis of the Co^{2+} formed or by weighing the $[(NH_3)_5CoOH_2]Br_3$ recovered. When the former method was used, the determination was done spectrophotometrically using concentrated HCl to develop the Co^{2+} color and relying on blanks to standardize the method.

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[1] R. K. Murmann, F. A. Posey, and H. Taube, *J. Am. Chem. Soc.*, **79**, 262 (1957).

[2] M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

[3] J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

[4] A. B. Lamb and K. J. Mysels, *ibid.*, **67**, 468 (1945).

[5] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952).

When $Ru(NH_3)_2^{2+}$ or Cr^{2+} was used as the reducing agent, the product solution contained Cr(III). This was separated from cobalt by oxidation in alkaline solution, using Br_2, and removal of cobalt oxide by filtration.

The isotopic composition of the oxygen in the Co(III) complex was determined as described elsewhere.[6] Measurements of isotopic ratios were made on an Atlas M86 mass spectrometer. The equation of Dostrovsky and Klein[7] was used to calculate the isotopic ratios. The value of $f = k_{16}/k_{18}$ was calculated from the equation[6]

$$f = \frac{\mathrm{d}\ln \mathrm{O}^{16}}{\mathrm{d}\ln \mathrm{O}^{18}} = \frac{\log \alpha(1 - N_e)/(1 - N_0)}{\log \alpha N_e/N_0} \approx \frac{\log \alpha}{\log \alpha N_e/N_0}$$

Here k_{16}/k_{18} represents the relative specific rates of the reductions for the two isotopic species, $\alpha = C_e/C_0$ denotes the fraction of the sample left unreduced, and N_0 and N_e are the values of the mole fractions of O^{18} in the complex initially and after partial reduction, respectively.

Results

The results of the experiments with a variety of reducing agents are shown in Table I. For the experiments shown here, the aquo salt was of normal isotopic composition, as was the solvent. Under these circumstances, and with the time of reaction short compared to the exchange half-life, effects arising from exchange are minimized, and unless there is substantial induced exchange (results to be described later show that the induced exchange is at most slight), the values of f can without complication be extracted from the experimental data. The experiments involving cathodic reduction were of greater duration than those in which chemical reducing agents were used, and for them the correction for spontaneous exchange is substantial, in some cases affecting the apparent value of f by as much as 4%. Since the exchange rate for the aquo ion is precisely known, it should be possible accurately to make allowance for it; the consistency of the values of f for the electrolytic experiments suggests that the correction procedure is satisfactory.

A series of experiments was also done using O^{18}-enriched $(NH_3)_5CoOH_2^{3+}$ in water of normal oxygen isotopic composition. Since the aquo ion and the solvent are not in isotopic equilibrium, a correction must be applied to the results for the spontaneous exchange.[8] The duration of reaction is short, so that the correction for the spontaneous exchange is slight and is small compared to the anomaly which the results feature. Except for the correction for spontaneous exchange, the results are treated like those in Table I, the final isotopic composition of the aquo ion being compared with that of aquo ion initially. For the latter determination the aquo complex was brought into solution and precipitated for analysis, but without reduction. The results obtained in the series of experiments with enriched aquo ion are shown in Table II.

TABLE I

THE VALUES OF f FOR THE REACTION OF VARIOUS REDUCING AGENTS WITH $(NH_3)_5CoOH_2^{3+}$ (AT 25°, OXIDANT ~0.09 M)

Reductant	Medium	$C_0/C_e = 1/\alpha$	N_e/N_0	Current density, ma cm^{-2}	f
Cr^{2+}	0.2 M H_2SO_4	6.7	1.106	...	1.056
$Ru(NH_3)_6^{2+}$	0.44 M HCl	2.4	1.0175	...	1.021
$Ru(NH_3)_6^{2+}$	0.44 M HCl	3.0	1.0235	...	1.021
V^{2+}	0.36 M $HClO_4$	3.1	1.022	...	1.020
V^{2+}	0.36 M $HClO_4$	3.1	1.022	...	1.020
V^{2+}	0.36 M $HClO_4$	3.5	1.0270	...	1.019
Eu^{2+}	0.36 M $HClO_4$	3.4	1.022	...	1.019
$Ru(NH_3)_6^{2+}$	0.8 M NH_3	3.5	1.020	...	1.017
$Cu(NH_3)_n^{+}$	0.8 M NH_3	3.2	1.030	...	1.026
$Cu(NH_3)_n^{+}$	0.8 M NH_3	4.5	1.034	...	1.023
$Eu(EDTA)^{2-}$	0.8 M NH_3	2.8	1.000	...	1.000
$Fe(EDTA)^{2-}$	0.8 M NH_3	3.2	0.998	...	0.998
$Cr(EDTA)^{2-}$	0.8 M NH_3	2.3	0.996	...	0.995
$Cr(EDTA)^{2-}$	0.8 M NH_3	2.6	0.996	...	0.996
$Cr(EDTA)^{2-}$	0.8 M NH_3	2.8	0.999	...	0.999
$Cr(EDTA)^{2-}$	0.36 M $HClO_4$	2.4	1.038	...	1.050
$Cr(EDTA)^{2-}$	0.36 M $HClO_4$	4.4	1.044	...	1.031
Pt gauze	0.57 M HCl	4.0	1.021	0.80	1.015
Pt gauze	0.57 M HCl	4.6	1.022	0.80	1.014
Pt gauze	1.40 M HCl	3.9	1.021	0.80	1.016
Cu sheet	0.36 M $HClO_4$	7.3	1.029	0.71	1.015
Cu wire	0.36 M $HClO_4$	4.2	1.021	2.0	1.015
Ag wire	0.36 M $HClO_4$	4.0	1.020	3.0	1.014
Cr sheet	0.36 M $HClO_4$	4.8	1.016	0.55	1.013
Cr sheet	0.36 M $HClO_4$	4.1	1.005	2.0	1.004
Cr sheet	0.36 M $HClO_4$	4.1	1.008	2.0	1.006
Ni sheet	0.36 M $HClO_4$	3.9	1.007	0.33	1.005
Fe[a] wire	0.36 M $HClO_4$	3.8	0.998	...	0.998

[a] Nonelectrolytic Fe reacts rapidly with $(NH_3)_5CoOH_2^{3+}$. The rate corresponds to a current density 10-fold higher than any reached in the electrolytic reductions.

TABLE II

THE APPARENT VALUES OF f FOR THE REDUCTION OF O^{18}-ENRICHED $(NH_3)_5CoOH_2^{3+}$ IN WATER OF NORMAL ISOTOPIC COMPOSITION[a]

Reductant	Temp, °C	(HCl), M[b]	$C_0/C_e = 1/\alpha$	N_e/N_0	Apparent f
$Ru(NH_3)_6^{2+}$	22–23	0.04	3.0	0.9685	0.972
Pr cathode[c]	1–2	0.58	2.3	0.9703	0.971
Pt cathode[c]	1–2	1.30	3.8	0.9629	0.973
Pt cathode[d]	22–23	0.57	2.7	0.9573	0.958
Pt cathode[d]	22–23	1.70	4.3	0.9563	0.970

[a] Aquo ion 5-fold enriched. [b] Initial concentration. [c] Current density = 8.0 ma cm^{-2}. [d] Current density = 0.80 ma cm^{-2}.

The values of f, if accepted at face value, would indicate that the complex containing H_2O^{18} reacts more rapidly than that with H_2O^{16}, contrary to reasonable expectation and contrary to the observations made with water of ordinary isotopic composition. A more likely explanation is that exchange of solvent water with the unreacted complex is induced by the oxidation–reduction reaction. Exchange would, of course, tend to deplete the complex in H_2O^{18} and produce an apparent value of f less than 1.00. The extent of exchange indicated by the data of Table II is so slight as not to affect significantly the results shown in Table I. Incorporation of 6% of solvent water would account for the discrepancy in f values for comparable experiments in Tables I and II; if the isotopic compositions of the solvent and complex differ by only 2%, as they do for the experiments of Table I, the isotopic

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[6] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

[7] I. Dostrovsky and F. S. Klein, *Anal. Chem.*, **24**, 414 (1952).

[8] H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2692 (1958).

composition of the residual aquo ion is not significantly modified by the induced exchange.

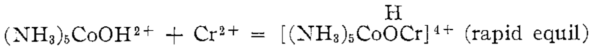
Discussion

The present results confirm the earlier ones[1] in showing that there is a large kinetic oxygen isotope effect of the reaction of Cr^{2+} with $(NH_3)_5CoOH^{2+}$ (under the conditions of the experiments the dominant path for the reduction involves the hydroxy rather than the aquo complex), and, if anything, f appears to be even somewhat larger than reported earlier. Dividing the observed value of f as recorded in Table I by the value of K expressing the isotopic discrimination in the equilibrium[9]

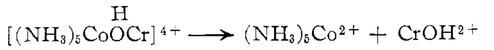
$$(NH_3)_5CoOH_2^{3+} = (NH_3)_5CoOH^{2+} + H^+ \qquad (1)$$

f for the reaction of Cr^{2+} with $(NH_3)_5CoOH^{2+}$ becomes 1.046, to be compared to 1.034 as reported earlier.

If the kinetic isotopic effect is interpreted in terms of the mechanism



$$(NH_3)_5CoOH^{2+} + Cr^{2+} = [(NH_3)_5Co\overset{H}{O}Cr]^{4+} \text{ (rapid equil)} \qquad (2)$$



$$[(NH_3)_5Co\overset{H}{O}Cr]^{4+} \longrightarrow (NH_3)_5Co^{2+} + CrOH^{2+} \qquad (3)$$

we must conclude that the effect of stretching the Co–O bond during the electron transfer in reaction 3 more than compensates for the effects in the opposite direction arising in reaction 2 out of bond formation between Cr and O and from residual vibrational modes in the activated complex. All in all, though the discrimination in reaction 2 is probably quite small,[10] the values of f observed show that the reduction of $(NH_3)_5CoOH^{2+}$ by Cr^{2+}(aq) calls for a great deal of weakening if not complete breaking of the Co–O bond in the activated complex.

When Eu^{2+}, V^{2+}, or $Ru(NH_3)_6{}^{2+}$ is the reducing agent in acid solution, the aquo ion rather than the hydroxy is the reactant. Thus the values of f recorded in Table I are not directly comparable to that calculated for Cr^{2+}. However, f for $Ru(NH_3)_6{}^{2+}$ reacting with $(NH_3)_5CoOH^{2+}$ has been measured as 1.017, and this result can be compared meaningfully to f = 1.04 as determined for Cr^{2+} with the same oxidizing agent. The coordination sphere of $Ru(NH_3)_6{}^{2+}$ remains intact when it is oxidized, and the activated complex for the reaction with $(NH_3)_5CoOH_2{}^{2+}$ is therefore of necessity of the outer-sphere type. A striking difference in the kinetic isotopic fractionation effect for the two types of mechanism is thus demonstrated by the results. The agreement of the values of f for the reaction of V^{2+}, Eu^{2+}, or $Ru(NH_3)_6{}^{2+}$ with $(NH_3)_5CoOH_2{}^{3+}$ suggests that these three reducing agents adopt similar mechanisms which, in view of the substitution inertia of $Ru(NH_3)_6{}^{2+}$, must be of the outer-sphere type. It should be mentioned that other evidence[11] has been adduced for the conclusion that the dominant path in the case of V^{2+}(aq) involves an outer-sphere activated complex.

The value of f for $Cu(NH_3)_n{}^+$ seems to be definitely in excess of that observed for $Ru(NH_3)_6{}^{2+}$ with $(NH_3)_5CoOH^{2+}$, but less than that for Cr^{2+}(aq). The fact that an e_g electron is being transferred, other things being equal, would appear to favor an inner-sphere mechanism.[12] Since the condition of substitution lability is met by $Cu(NH_{3n})_n{}^+$, it is on the whole somewhat surprising that the value of f is not in the same range as is observed for Cr^{2+}. Possibly the reaction is so rapid as to be almost diffusion controlled, and this would lower the value of f, and it is of course also possible that both inner- and outer-sphere mechanisms operate in this case.

With the reducing agents $Eu(EDTA)^{2-}$, Fe$(EDTA)^{2-}$, and $Cr(EDTA)^{2-}$ in alkaline solution, f is very close to 1.000. For one member of this group, $Fe(EDTA)^{2-}$, the rate of reaction was measured.[13] Although the reaction is very rapid, the second-order specific rate being $1.2 \times 10^6\ M^{-1}\ sec^{-1}$ at 25°, the rate is not diffusion controlled. The value of f measured for $Fe(EDTA)^{2-}$ shows, however, that stretching the Co–OH bond is not important in the rate-determining step. We suggest that the reaction proceeds by an inner-sphere activated complex—a rate as high as 10^6 by an outer-sphere mechanism for a reducing agent such as $Fe(EDTA)^{2-}$ which undoubtedly undergoes large changes in geometry on being oxidized seems quite impossible—and that in this case substitution on Fe(II) is rate determining[14] and this conclusion may apply also to the other EDTA complex in alkaline solution. The rate observed is of a magnitude to be compatible with this assumption. It should be noted that Cr(II) in the presence of EDTA in acidic solution gives large values of f, in contrast to the behavior in alkaline solution. We are unable to offer a satisfactory explanation for this difference. An *ad hoc* assumption to account for it is this: we suggest that in alkaline solution, all coordination positions are taken up by groups derived from EDTA, and the rate of bond opening is relatively slow, while in acidic solution, the ligand is partly protonated, thus leaving one or more water molecules associated with the complex. The results of Pecsok, *et al.*,[15] show that below pH 4 at least one molecule of water is associated with Cr^{2+}, and they leave open the possibility that at pH values as low as obtained in our experiments, the metal ion is completely uncomplexed.

The similarity between the reduction of ammine-

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[9] H. R. Hunt and H. Taube, *J. Phys. Chem.*, **63**, 124 (1959).

[10] The equilibrium quotient governing O^{16}–O^{18} exchange between Mg$(H_2O)_6{}^{2+}$ and H_2O is 1.010 (H. M. Feder, Ph.D. Dissertation, University of Chicago, 1954); in a binuclear intermediate, if formed in the reaction, the Cr–O bond is probably long so that the discrimination will be even less than for $Mg(H_2O)_6{}^{2+}$–H_2O exchange.

[11] P. Dodel and H. Taube, *Z. Physik. Chem.* (Frankfurt), **44**, 92 (1965).

[12] H. Taube, Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research VI, "Topics in Modern Inorganic Chemistry," W. O. Milligan, Ed., Houston, Texas, 1963, p 7.

[13] We are indebted to Mr. Harry Price for making the measurement of rate.

[14] The suggestion has been offered [J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965)] that substitution on Cr^{2-} may be rate determining in the reaction of Cr^{2+} with $(NH_3)_5CoX^{2-}$. The reaction of Cr^{2+} with $(NH_3)_5CoOH^{2+}$ is as rapid as the reaction of present interest; arguments against the rate being governed by substitution in the case of the Cr^{2+} reaction are advanced in ref 2.

[15] R. L. Pecsok, L. D. Shields, and W. P. Schaeffer, *Inorg. Chem.*, **3**, 114 (1964).

cobalt(III) complexes at the dropping-Hg electrode and by outer-sphere reducing agents has already been pointed out.[16,17] The results in Table I suggest that the similarity extends, at least for $(NH_3)_5CoOH_2^{3+}$ as oxidant, to the metals Pt, Cu, Ag, and possibly Cr acting as cathode. For Cu *f* is independent of the current density, and in this case at least it is fairly certain that *f* is characteristic of the electrode process rather than of the diffusion step. When diffusion to the electrode is rate limiting, a value of *f* very close to 1.000 is expected. The data for Cr in fact show a variation of *f* with current density and suggest that at the higher current densities, diffusion to the electrode becomes rate limiting. It is difficult to understand why the limiting diffusion current at the Cr electrode is less than at Pt, Cu (and apparently Ag), and we can only suppose that there was a difference in experimental arrangement, perhaps having to do with the rate of stirring. This value is fairly close to that observed for the reductants $Ru(NH_3)_6^{2+}$, V^{2+}, and Eu^{2+} which we take to react by outer-sphere activated complexes. The Ni cathode appears to behave differently from the others. We have no reason to set aside this result but, since only a single experiment with Ni was done, are not prepared to assert that this electrode is really different.

Metallic iron reduces the aquopentaamminecobalt(III) complex directly and at a rate so great that the reaction must be diffusion controlled. The value of *f* is observed to be close to 1.00, as would be expected for a diffusion-controlled process.

The most significant of the results reported by us may well be those contained in Table II. As has already been mentioned, they suggest that the electron-transfer reactions induce exchange between $(NH_3)_5CoOH_2^{3+}$ and solvent. This implies that the cobalt(II) complex which is formed on electron transfer lasts long enough to undergo water exchange with the solvent and electron transfer with Co(III).

$$(NH_3)_5CoOH_2^{3+} + e^- \longrightarrow (NH_3)_5CoOH_2^{2+}$$

$$(NH_3)_5CoOH_2^{2+} + H_2O^* \longrightarrow (NH_3)_5CoO^*H_2^{3+} + H_2O$$

$$(NH_3)_5CoOH_2^{2+} + (NH_3)_5CoOH_2^{3+} \longrightarrow (NH_3)_5CoOH^*H_2^{3+} + (NH_3)_5CoOH_2^{2+}$$

The effect merits further investigation and we plan to work on this aspect of the subject.

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(16) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(17) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 427 (1965).

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Kinetics of Substitution Reactions of Some Monosubstituted Derivatives of Nitrosyltricarbonylcobalt(0)[1]

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Compounds of the type $CoNO(CO)_2L$, where L = CO, CNC_6H_{11}, $As(C_6H_5)_3$, $P(OCH_2)_3CCH_3$, $P(OC_6H_5)_3$, $P(OCH_3)_3$, and $P(C_6H_5)_3$, undergo L group substitution in the presence of phosphines to give $CoNO(CO)_2L'$. The reactions at 40.4° proceed at slow to moderate rates and are dependent upon the nature and concentration of L′. For the same substrate $CoNO(CO)_2L$, the rates of reaction increase with changes in reagent L′ in the order: $P(OC_6H_3)_3 < P(C_6H_5)_3 < P(C_6H_5)_2C_2H_5 < P(n\text{-}C_4H_9)_3$. For the same reagent but different substrates the rates of reaction increase with changes in L in the order: $P(C_6H_5)_3 < P(OCH_3)_3 < P(OC_6H_5)_3 < As(C_6H_5)_3 \sim P(OCH_2)_3CCH_3 < CNC_6H_{11} << CO$. The reaction of $CoNO(CO)_2L$ with L to give $CoNO(CO)L_2$ and CO at 40.4° proceeds more slowly than L group exchange and is also dependent upon the nature and concentration of L. The results are compared and contrasted to the $Ni(CO)_2L_2$ system,[2] and the nature of the bonding between metal and L group in both systems is discussed.

Introduction

The monosubstituted derivatives of $CoNO(CO)_3$ might be expected to exhibit kinetic behavior similar to that of the disubstituted derivatives of $Ni(CO)_4$, since the two systems are structurally and electronically similar. Meriwether and Fiene[2] have found that compounds of the type $Ni(CO)_2L_2$ in the presence of a phosphine undergo ligand exchange more rapidly than additional CO substitution. Furthermore, all reactions involving derivatives of $Ni(CO)_4$ were found to be first order in complex and independent of the added phosphine. Work has also been reported on the reaction of $Ni(CO)_4$ with L to give $Ni(CO)_3L$[3] and thence

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[1] Taken in part from the Ph.D. Thesis of E. M. T., Northwestern University, 1966.

[2] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 3200 (1959).

[3] (a) F. Basolo and A. Wojcicki, *ibid.*, **83**, 520 (1961); (b) R. F. Heck, *ibid.*, **85**, 657 (1963); (c) L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *ibid.*, **88**, 2334 (1966).