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Kinetics of the Formation of Cobalt–Rhodium Heptacarbonyl

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The kinetics of the reaction $Co_2Rh_2(CO)_{12} + 2CO \rightarrow 2CoRh(CO)_7$ have been studied at $T = 267$–294 K and at $P_{CO} = 0.05$–0.20 MPa ($8.7 \times 10^{-4} - 4.8 \times 10^{-3}$ mole fraction) in *n*-hexane as solvent. The rate of the reaction was found to be first order in the mixed-metal cluster $Co_2Rh_2(CO)_{12}$ (1) and to be consistent with the two-term rate expression rate = $\{k_1 + k_2[CO]\}[Co_2Rh_2(CO)_{12}]$, where the term $k_1[Co_2Rh_2(CO)_{12}]$ represents the single most important contribution to the overall rate of cluster fragmentation under the present reaction conditions. The activation parameters determined from 20 experiments are $\Delta H^{*}_1 = 60.6 \pm 1.9$ kJ/mol (14.5 ± 0.4 kcal/mol), $\Delta S^{*}_1 = -80.3 \pm 6.7$ J/(mol K) (-19.2 ± 1.6 cal/(mol K)) and $\Delta H^{*}_2 = 53.3 \pm 6.6$ kJ/mol (12.7 ± 1.6 kcal/mol), $\Delta S^{*}_2 = -64.4 \pm 23.5$ J/(mol K) (-15.4 ± 5.6 cal/(mol K)). It is proposed that two independent reaction pathways are available for the transformation of $Co_2Rh_2(CO)_{12}$ (1) to $CoRh(CO)_7$ (2) and that these are characterized by (I) an intramolecular activation of $Co_2Rh_2(CO)_{12}$ and (II) either (a) the bimolecular reaction of $Co_2Rh_2(CO)_{12}$ with CO or (b) the unimolecular reaction of a preequilibrated species $\{Co_2Rh_2(CO)_{13}\}$, as the rate-determining steps.

Introduction

A variety of homometallic[2,3] as well as mixed-metal[4,5] carbonyl clusters undergo reactions with carbon monoxide to yield lower nuclearity species (eq 1), and this reduction

$$M_m(CO)_n + xCO \rightleftharpoons \sum \nu_i (M_m(CO)_n)_i \qquad (1)$$

in nuclearity[6] is often fully reversible. Numerous examples of reversibility, especially from group VIII (Co, Rh, Ir) clusters exist,[7] and two relevant examples in the present context are the reactions of $Co_4(CO)_{12}$[7a] and $Rh_4(CO)_{12}$[7b] with carbon monoxide respectively to yield the corresponding dinuclear carbonyls. Such "model" transformations of metal clusters, resulting in the cleavage of metal–metal bonds, have received continued interest for synthetic,[2-5] thermodynamic,[7,8] and kinetic and mechanistic[9] reasons. A general stoichiometric equation representing these cluster transformations, where only carbonyl ligands are involved, can be written as in eq 1.

These model transformations should not be considered simple or elementary in the kinetic sense. Indeed, the complexity of the reactions, i.e. the numerous metal–metal bonds broken and M–CO bonds formed, prohibits such a superficial classification. Hence, for the most part, kinetic studies are restricted to identifying the primary or salient features characterizing the reduction in nuclearity. A preequilibrium could be such a feature, as was shown in the transformation of $Co_4(CO)_{12}$. The high-pressure CO kinetic data were consistent with the formation of an intermediate with the stoichiometry $\{Co_4(CO)_{13}\}$:[9a]

$$Co_4(CO)_{12} + CO \rightleftharpoons \{Co_4(CO)_{13}\} \qquad (2)$$

The mixed-metal cluster $Co_2Rh_2(CO)_{12}$ (1) has been shown to react rapidly with dissolved carbon monoxide at 273 K in *n*-hexane to give the dinuclear species $CoRh(CO)_7$ (2).[10] At very low partial pressures of carbon monoxide ($P_{CO} < 0.05$ MPa), measurable concentrations of both the species $Co_2Rh_2(CO)_{12}$ (1) and $CoRh(CO)_7$ (2) coexist in solution. The equilibria for this reaction have been extensively studied at very low partial pressures $P_{CO} = 0.005$–0.050 MPa and at $T = 258$–288 K and the experimentally determined Gibbs free energy of reaction $\Delta_r G^\circ(293\text{ K})$ was found to be -16.8 kJ/mol:[11]

$$\underset{\mathbf{1}}{Co_2Rh_2(CO)_{12}} + 2CO \rightleftharpoons \underset{\mathbf{2}}{2CoRh(CO)_7} \qquad (3)$$

In the present paper, the kinetics of the formation of $CoRh(CO)_7$ (2) from $Co_2Rh_2(CO)_{12}$ (1) and dissolved carbon monoxide in *n*-hexane (eq 3) are examined. Specifically, the kinetics between $T = 267$–294 K and $P_{CO} = 0.05$–0.20 MPa were studied in order to determine the reaction orders in (i) the tetranuclear cluster $Co_2Rh_2(CO)_{12}$ (1) and (ii) dissolved carbon monoxide and to determine the parameters of activation. Under these partial pressures and temperatures, the influence of the reverse reaction on the overall kinetics can be neglected. The equilibrium is shifted entirely in favor of $CoRh(CO)_7$ (2) (conversions ≥98%).

Experimental Section

General Information. All solution preparations and transfers were carried out under a nitrogen (99.995%, Pan Gas, Luzern, Switzerland) or argon (99.998%, Pan Gas, Luzern, Switzerland)

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[1] Deceased July 9, 1989.

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atmosphere by using standard Schlenk techniques.[12] The cluster $Co_2Rh_2(CO)_{12}$ (1) was prepared from $NaCo(CO)_4$ and $Rh_2(CO)_4Cl_2$ in *n*-hexane.[10] Elemental analyses of recrystallized 1 gave 21.7% carbon and 31.1% rhodium (courtesy of Ciba-Geigy AG, Basel, Switzerland). The calculated values are 21.8% carbon and 31.2% rhodium. *n*-Hexane (Puriss quality, Fluka AG, Buchs, Switzerland) was refluxed from sodium potassium alloy under nitrogen. The carbon monoxide used for reaction 3 was produced at the ETH-Z (and stored in aluminum cylinders).

Kinetic studies were performed in a 1.5-L stainless steel (SS316) autoclave (Büchi-Uster, Switzerland), which was connected to a high-pressure infrared cell. The autoclave (to 22.5 MPa) was equipped with a packed magnetic stirrer with six bladed turbines in both the gas and liquid phases (Autoclave Engineer, Erie, PA) and was constructed with a heating/cooling mantel. A high-pressure membrane pump (Model DMK30, Orlita AG) with a maximum rating of 32.5 MPa and 3-L/h flow rate was used to circulate the *n*-hexane solutions from the autoclave to the high-pressure IR cell and back to the autoclave via jacketed $^1/_8$-in. (SS316) high-pressure tubing (Autoclave Engineers, Erie, PA). The entire system, autoclave, transfer lines, and infrared cell, was cooled by using a Lauda RX20 cryostat and could be maintained isothermal (ΔT = 0.5 °C) in the range −20 °C to 40 °C. Temperature measurements were made at the cryostat, autoclave, and IR cell with Pt-100 thermoresistors. The necessary connections to vacuum and gases were made with $^1/_4$-in. (SS316) high-pressure tubing (Autoclave Engineers), and a 1.000-MPa (3 place accuracy) piezocrystal was used for pressure measurements (Keller AG, Wintertur, Switzerland). The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell (SS316) was constructed at the ETH-Z and could be heated or cooled. The NaCl (Korth) and KBr (Korth) and silicon (ETH-Z) windows used had dimensions of 40-mm diameter by 15-mm thickness. Two sets of viton and silicon gaskets provided sealing, and Teflon spacers were used between the windows. The flow-through IR cell[13a] is a variation of a design originally due to Noack[13b] and differs in some respects with other high-pressure infrared cells described in the literature (for a review see ref 13g). The high-pressure cell was situated in a Perkin-Elmer PE983 infrared spectrophotometer equipped with a Model 3600G data station. Spectra were recorded with a 0.22-mm slit width. Details of the equipment and IR cell can be found elsewhere.[14]

The tetranuclear carbonyl $Co_2Rh_2(CO)_{12}$ (1) has absorbance maxima at 2074, 2064, 2059, 2038, 2030, 1910, 1885, 1871, and 1858 cm^{-1} in the infrared,[15] and the dinuclear carbonyl $CoRh(CO)_7$ (2) has absorbance maxima[10] at 2134, 2064, 2058, 2049, 2006, 1977, and 1955 cm^{-1}. The determined extinction coefficient at 1955 cm^{-1} for $CoRh(CO)_7$ (1) is $\epsilon(1955)$ = 2950 L/(mol cm) with a slit width of 0.22 mm. The extinction coefficient of *n*-hexane at 1138 cm^{-1} is $\epsilon(1138)$ = 2.353 L/(mol cm), also at a slit width of 0.22 mm. From the Lambert Beer law, the in situ concentration of $CoRh(CO)_7$ (2) in units of mole fractions $x(CoRh(CO)_7)$ can be directly measured in the low-pressure kinetic experiments with a high degree of accuracy by using eq 4, where A is the absorbance.

$$x(CoRh(CO)_7) = A(1955)\epsilon(1138)/A(1138)\epsilon(1955) \qquad (4)$$

When eq 4 is applied, the mole fraction of dissolved carbon monoxide is understood to approach zero.[16] Infrared spectra of the species $CoRh(CO)_7$ have already appeared in the literature.[10,11,14]

Kinetic Studies. General Procedures. A 33-mg amount of $Co_2Rh_2(CO)_{12}$ (1) was dissolved in 200 mL of *n*-hexane (3.25 × 10^{-5} mole fraction) in a Schlenk tube under a nitrogen atmosphere, and the solution was transferred via a $^1/_8$-in. inlet line into the evacuated and thermostated autoclave. Depending on the system temperature, the total pressure in the autoclave, i.e. the vapor pressure of *n*-hexane plus a low partial pressure of nitrogen, was P_T = 0.01–0.03 MPa. More nitrogen was added to give a total system pressure of 0.4 MPa. The stirring speed was 400 rpm. During this time, the high-pressure membrane pump continuously circulated the *n*-hexane solution from the autoclave to the high-pressure infrared cell and back to the autoclave. Full in situ infrared spectra were taken from 2200 to 1800 cm^{-1} and from 1300 to 1100 cm^{-1}. Little to no additional noise could be identified in the in situ spectra as the solution was pumped (10 cm/s) through the high-pressure infrared cell.

Kinetics: Variation of CO and Variation of Temperature. A total of 20 experiments were carried out at four different carbon monoxide partial pressures (P_{CO} = 0.05, 0.10, 0.15, 0.20 MPa) and at four different temperatures (T = 267, 276, 285, 294 K). At a time t = 0, with the membrane pump running, carbon monoxide (0.05–0.20 MPa) was added to the system containing $Co_2Rh_2(CO)_{12}$ (1) and *n*-hexane solution. The in situ measured absorbance at 1955 cm^{-1} was then measured every 10 s for 60 min. At the end of the 60 min, full in situ spectra were recorded from 2200 to 1800 cm^{-1} and from 1300 to 1100 cm^{-1}. The appearance of $CoRh(CO)_7$ rather than the disappearance of $Co_2Rh_2(CO)_{12}$ was measured in the present kinetic study, since the accuracy of measuring the absorbance at 1955 cm^{-1} far exceeds the accuracy of measuring the absorbance at 1873 cm^{-1}, given the respective extinction coefficients for these bands.

Equation 5 was used for the temperature-dependent Henry constant H_{CO} in *n*-hexane at low partial pressures of carbon monoxide (i.e. in the limit as P_{CO} approaches 0), where P_{sat} is the

$$\ln (H/P_{sat}) = -1.46 + 2840/T \qquad (5)$$

saturated partial pressure of the solvent *n*-hexane and the temperature T is given in degrees Kelvin.[14] The equation was developed from experimental data collected in the same temperature range. The form of this temperature-dependent Henry constant comes from Johna,[17] and the saturated vapor pressure of *n*-hexane as a function of temperature can be found in the literature.[18] Since the experiments are conducted on the limited total pressure interval 0.45–0.65 MPa, the Krichevsky–Kasarnovsky modification to the Henry constant has not been used.[19]

In terms of short-term transient effects, (a) approximately 15 s was required to achieve the carbon monoxide pressure jump ΔP ($\Delta P = P_i$) in the stirred autoclave, (b) approximately 30 s was required before the solution was essentially saturated with dissolved carbon monoxide, and (c) a 30–40-s delay existed between the time at which events in the stirred autoclave occurred and the time at which the corresponding event could be measured at the spectrophotometer. The experimentally measured overall mass transfer coefficient K_La for carbon monoxide into *n*-hexane in the present apparatus at 200 rpm was K_La = 0.06/s.[14] This was determined by using the method of Deimling.[20] The effect of the transient effects on the quality of the kinetic data obtained for pseudo-first-order reactions with half lives $t_{0.5} \geq 4$ min was considered negligible.

Results

Effect of Carbon Monoxide. Five sets of experiments were performed, and in each set, the partial pressure of CO was systematically varied (P_{CO} = 0.05, 0.10, 0.15, 0.20 MPa). The in situ concentrations of $CoRh(CO)_7$ (2) for

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(16) In general, concentrations in moles per liter are not directly measurable quantities in most high-pressure IR cells because there is cell expansion and the volumetric properties of most hydrocarbon solvents under finite dissolved gas concentrations are rarely known.

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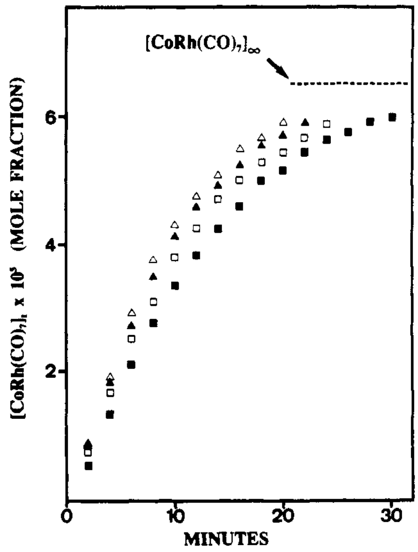

Figure 1. Effect of carbon monoxide on the rate of formation of CoRh(CO)$_7$ (2) at 276 K starting with $Co_2Rh_2(CO)_{12}$ (1) under (■) 0.05, (□) 0.10, (▲) 0.15, and (△) 0.20 MPa of CO.

one set of experiments performed at 276 K are shown in Figure 1. Clearly, there is only a marginal increase in the rate of cluster fragmentation due to increases in the CO partial pressure. Further, it should be noted that quantitative conversion of $Co_2Rh_2(CO)_{12}$ to CoRh(CO)$_7$ occurred in all four experiments within the 60-min reaction period (complete conversion corresponds to 6.5 × 10^{-5} mole fraction).

During reaction, there were no unidentified infrared absorbencies in the measured region 2200–1800 cm^{-1}. Indeed, only ν(M–CO) infrared absorption bands attributed to $Co_2Rh_2(CO)_{12}$ (1) and CoRh(CO)$_7$ (2) were observed to change in intensity. A very low concentration of $Rh_4(CO)_{12}$ (roughly 2–3%), an impurity from the $Co_2Rh_2(CO)_{12}$ starting material was always present from the beginning of the experiments. The reaction is very selective.

Assuming that the formation of CoRh(CO)$_7$ (2) is first order in the tetranuclear carbonyl $Co_2Rh_2(CO)_{12}$ (1), the data presented in Figure 1 can be analyzed in accordance with eqs 6 and 7. At this point, no assumptions have been made concerning the CO dependence of the observed rate constant k_{obs}.

$$d[Co_2Rh_2(CO)_{12}]/dt = -k_{obs}[Co_2Rh_2(CO)_{12}] \quad (6)$$

$$\ln ([Co_2Rh_2(CO)_{12}]_t/[Co_2Rh_2(CO)_{12}]_0) = -k_{obs}t \quad (7)$$

The experimental data presented in Figure 1 were transformed according to eq 7. Straight lines were obtained for each data set, as shown in Figure 2. Therefore, under the present reaction conditions, the cluster fragmentation is first order in the concentration of the tetranuclear complex $Co_2Rh_2(CO)_{12}$ (1). Regression of the data over at least 2 half-lives gave the rate constants k_{obs} as (1.49 ± 0.04) × 10^{-3}, (1.61 ± 0.02) × 10^{-3}, (1.84 ± 0.02) × 10^{-3}, and (2.02 ± 0.03) × 10^{-3} s^{-1} under 0.05, 0.10, 0.15, and 0.20 MPa (1.07 × 10^{-3}, 2.15 × 10^{-3}, 3.22 × 10^{-3}, 4.29 × 10^{-3} mole fraction) of carbon monoxide, respectively.[21a] The small intercept at 40 s on the x axis corresponds to the delay interval between events at the reactor and the time at which these events arrive at the spectrophotometer.

Effect of Temperature. The results of all five sets of experiments, as a function of temperature and as a function of CO liquid-phase mole fraction, are shown in Figure 3. The open and closed symbols represent experiments performed more than 2 weeks apart and with different n-hexane solvent. The two sets of data reported at 276 K indicate the excellent reproducibility of the results.

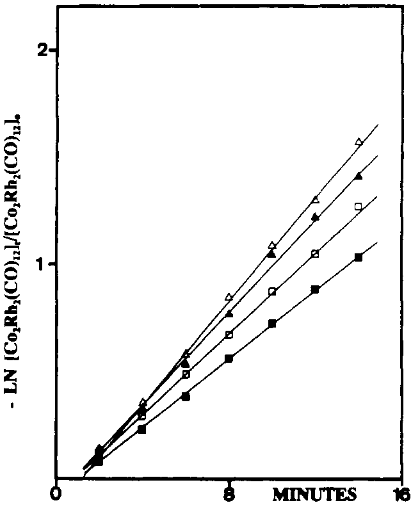

Figure 2. Effect of carbon monoxide on the rate constant k_{obs} for the formation of CoRh(CO)$_7$ (2) at 276 K starting with $Co_2Rh_2(CO)_{12}$ (1) under (■) 0.05, (□) 0.10, (▲) 0.15, and (△) 0.20 MPa of CO.

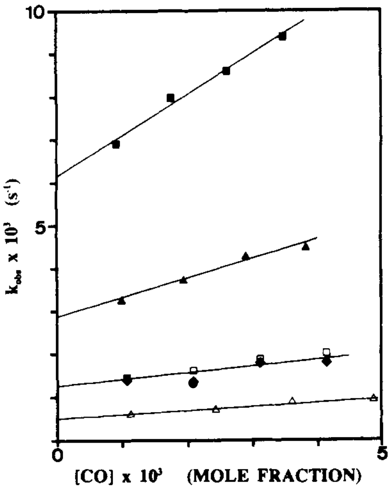

Figure 3. Observed rate constants k_{obs} as a function of temperature for the reaction of $Co_2Rh_2(CO)_{12}$ (1) to form CoRh(CO)$_7$ (2) at (△) 267 K, (□ and ◆) 276 K, (▲) 285 K, and (■) 294 K.

The results presented in Figure 3 are consistent with a two-term expression for the observable rate constant k_{obs}. The two-term rate expression is given in eq 8, where the

$$d[Co_2Rh_2(CO)_{12}]/dt = -\{k_1 + k_2[CO]\}[Co_2Rh_2(CO)_{12}] \quad (8)$$

rate constant k_1 corresponds to a first-order reaction pathway (I) and where the rate constant k_2 corresponds to a second-order pathway (II). Further, it is clear from Figure 3 that the term k_1 is of considerable importance to the overall rate of cluster fragmentation. The numerical values of the rate constants were k_1(267 K) = (4.53 ± 0.5) × 10^{-4} s^{-1}, k_1(276 K) = (1.25 ± 0.09) × 10^{-3} s^{-1}, k_1(285 K) = (2.88 ± 0.14) × 10^{-3} s^{-1}, and k_1(294 K) = (6.15 ± 0.16) × 10^{-3} s^{-1} for reaction pathway I and k_2(267 K) = (1.02 ± 0.16) × 10^{-1} s^{-1} (mole fraction)$^{-1}$, k_2(276 K) = (1.58 ± 0.32) × 10^{-1} s^{-1} (mole fraction)$^{-1}$, k_2(285 K) = (4.35 ± 0.53) × 10^{-1} s^{-1} (mole fraction)$^{-1}$, and k_2(294 K) = (9.45 ± 0.66) × 10^{-1} s^{-1} (mole fraction)$^{-1}$ for reaction pathway II.[21b]

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(21) (a) Errors are reported as standard deviations. (b) An unweighted linear regression was performed at each temperature to obtain the rate constants $k_1(T)$ and $k_2(T)$.

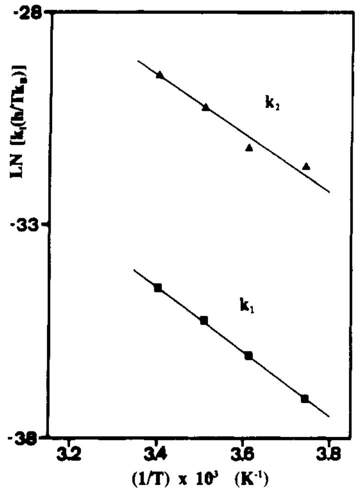

Figure 4. Effect of temperature on the rate constants k_1 and k_2.

The temperature dependences of the rate constants k_1 and k_2 are shown in Figure 4. The apparent activation parameters for the two reaction pathways are $\Delta H^{\ddagger}_1 = 60.6 \pm 1.9$ kJ/mol (14.5 ± 0.4 kcal/mol), $\Delta S^{\ddagger}_1 = -80.3 \pm 6.7$ J/(mol K) (-19.2 ± 1.6 cal/(mol K)) and $\Delta H^{\ddagger}_2 = 53.3 \pm 6.6$ kJ/mol (12.7 ± 1.6 kcal/mol), $\Delta S^{\ddagger}_2 = -64.4 \pm 23.5$ J/(mol K) (-15.4 ± 5.6 cal/(mol K)).[22]

Discussion

Reaction Pathway I. The first-order term $k_1[Co_2Rh_2(CO)_{12}]$ strongly suggests the existence of a reaction pathway characterized by the intramolecular activation of $Co_2Rh_2(CO)_{12}$ as the rate-determining step (eq 9). Such

$$\underset{1}{Co_2Rh_2(CO)_{12}} \xrightarrow{k_1} \{Co_2Rh_2(CO)_{12}\}^* \rightarrow \ldots\ \underset{2}{2CoRh(CO)_7} \tag{9}$$

activation can be assumed to give rise to a highly reactive intermediate i.e. $\{Co_2Rh_2(CO)_{12}\}^*$, where at least one metal–metal bond is cleaved and which undergoes further reaction with CO. Indeed, it appears very difficult to identify a rational first-order mechanism that does not require the intramolecular cleavage of a metal–metal bond. Similarly, coordinatively unsaturated open polyhedrons have been proposed as intermediates in a variety of metal cluster transformations.[23a] Other examples include the cleavage of one Mn–Fe bond in $Cp(CO)_2MnFe_2(CO)_6(\mu\text{-}PPh)$[23b] and the cleavage of the Fe–Co bond in $(\mu\text{-}MeP)FeCoWCp(CO)_8$.[23c]

The unexpected negative entropy of activation is perhaps explained in terms of the two possible isomers of $Co_2Rh_2(CO)_{12}$ (Figure 5). It is known that the mixed-metal cluster $Co_2Rh_2(CO)_{12}$ has a structure with three bridging CO ligands in the basal plane,[15] similar to the homometallic analogues $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$.[24,25] Further, on the basis of spectroscopic evidence, it is strongly believed that structure "A" with two rhodium atoms in the basal plane is by far the predominant isomer.[15] The minor isomer "B" has a higher free energy and very likely a lower entropy (both isomers have the same number of M–M and M–CO bonds as contributions to the total enthalpy of the clusters). Thus, it is the minor but more reactive isomer B that reacts via the intramolecular pathway and gives rise to the apparent negative entropy of activation due to rapid equilibrium exchange with the observable isomer A. This reasoning might also suggest the preferential cleavage of the Rh–Rh bond in isomer B.

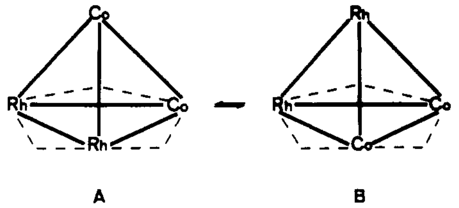

Figure 5. Predominant isomer "A" and minor isomer "B" for $Co_2Rh_2(CO)_{12}$.[15]

Reaction Pathway II. The second-order term $k_2[Co_2Rh_2(CO)_{12}][CO]$ implies a reaction pathway characterized by either (i) the direct bimolecular reaction of $Co_2Rh_2(CO)_{12}$ with CO, and hence a ligand-assisted cleavage of the tetrahedron, or (ii) the unimolecular reaction of a preequilibrated species of the stoichiometry $\{Co_2Rh_2(CO)_{13}\}$ as the rate-determining step. In eq 10, the

$$\underset{1}{Co_2Rh_2(CO)_{12}} + CO \overset{k_i}{\rightleftharpoons} \{Co_2Rh_2(CO)_{13}\} \xrightarrow{k_j} \ldots\ \underset{2}{2CoRh(CO)_7} \tag{10}$$

simplest representation for this second-order reaction pathway is presented, where the intermediate $\{Co_2Rh_2(CO)_{13}\}$ may or may not be in equilibrium with $Co_2Rh_2(CO)_{12}$ (1) depending on the relative magnitude of the rate constants k_i, k_{-i}, and k_j.

An open polyhedron where one of the two potential coordination sites is occupied by CO would represent a more probable geometry for an intermediate of the stoichiometry $\{Co_2Rh_2(CO)_{13}\}$. Of course, questions concerning which metal–metal bond was broken arise. Further, the term $k_2[Co_2Rh_2(CO)_{12}][CO]$ could represent more than one particular reaction pathway given the heteronuclear nature of complexes considered.

Generalized Rate Constant k_{obs}. An important result of this study has been to show that a significant first-order process, namely that represented by the term $k_1[Co_2Rh_2(CO)_{12}][CO]^0$, can exist for the fragmentation of a pure metal carbonyl cluster in the presence of CO. For the present reaction, a simple two-term expression (eq 8) was sufficient to describe the overall kinetics.

Finally, after consideration of the significant first-order and second-order terms obtained in this study as well as (i) the second-order term observed for the fragmentation of $H_2FeRu_3(CO)_{13}$ and $H_2Ru_4(CO)_{13}$ with carbon monoxide[4a,c] and (ii) the second- and third-order terms observed for the fragmentation of $Co_4(CO)_{12}$ under carbon monoxide,[9a] we note that a more general expression for k_{obs} for the fragmentation of pure metal carbonyl clusters under carbon monoxide may be valid (eq 11). This equation

$$k_{obs} = \{k_1 + k_2[CO] + k_3[CO]^2\} \tag{11}$$

allows for (a) intramolecular rate-determining steps (primarily k_1) and (b) the ligand-assisted cleavage of metal–metal bonds (primarily but not exclusively k_2), as well as (c) cluster preequilibria (in k_2 and k_3). Further, it is realized that this equation has particular relevance in the

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[22] Significant errors in the numerical values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ arise for 2nd and higher order reactions when concentrations are expressed in molarities or molalities, as shown by: (a) Guggenheim, E. A. *Trans. Faraday Soc.* **1937**, *33*, 607. (b) Hepler, L. G. *Thermochim. Acta* **1981**, *50*, 69. (c) Hamann, S. D.; le Noble, W. J. *J. Chem. Educ.* **1984**, *61*, 658.

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case of heteronuclear clusters, where each term is, in the strict sense, a summation over a number of possible reaction pathways.

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Supplementary Material Available: Tables of $[CoRh(CO)_7]_t$ versus time data and a table of $k_{obs}(T,x_{H_2})$ data (4 pages). Ordering information is given on any current masthead page.

Electron Transfer between Mononuclear Metal Carbonyl Anions ($M(CO)_5^-$, M = Mn, Re; $CpFe(CO)_2^-$; $CpM(CO)_3^-$, M = Cr, Mo) and Trinuclear Clusters ($M_3(CO)_{12}$, M = Fe, Ru, Os) and between Trinuclear Dianions ($M_3(CO)_{11}^{2-}$, M = Fe, Ru, Os) and Metal Carbonyl Dimers ($Mn_2(CO)_{10}$ and $Cp_2M_2(CO)_6$, M = Cr, Mo, W)

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Reaction of mononuclear metal carbonyl anions with trinuclear clusters of group 8 ($M_3(CO)_{12}$, M = Fe, Ru, Os) at ambient conditions leads to four separate outcomes: (1) formation of the metal carbonyl dimer and the trinuclear dianion which occurs whenever the two-electron reduction potential for the dimer is more negative than for the trinuclear cluster, (2) formation of $MFe_2(CO)_7^-$ by elimination of $Fe(CO)_5$ which occurs for M = $Re(CO)_5$, $Mn(CO)_5$, and $CpMo(CO)_3$, (3) formation of the adduct, $MRu_3(CO)_{11}^-$, which occurs for $Re(CO)_5$, and (4) no reaction when the two-electron reduction potential for the trinuclear complex is more negative than for the dimer. For complexes where the two-electron potential for the cluster is more negative than for the dimer, reaction of $M_3'(CO)_{11}^{2-}$ with M_2 to give $M_3'(CO)_{12}$ and $2M^-$ is observed. The observed reactions allow an estimate of the two-electron reduction potentials for the trinuclear clusters. The kinetics of all of these reactions indicate a first-order dependence on the oxidant and on the reductant and are most consistent with outer-sphere electron transfer.

Reaction of anionic carbonyl species with metal cluster complexes has been among the most useful synthetic procedures to high nuclearity and mixed-metal clusters.[1,2] The reaction of cluster anions with cluster complexes to generate high nuclearity clusters has been termed redox condensation.[1]

$$Rh_6(CO)_{15}^{2-} + Rh_6(CO)_{16} \rightarrow Rh_{12}(CO)_{30}^{2-} \rightarrow CO \quad (1)$$

Such reactions are used synthetically, but the mechanisms have not been investigated.

Several reactions of mononuclear carbonyl anions with metal clusters have been examined for synthetic applications. The reaction of $Fe(CO)_4^{2-}$ with $M_3(CO)_{12}$ (M = Fe, Ru, Os) is a synthetic route to the mixed-metal tetranuclear cluster dianions.[2] The reaction of monoanions, $M(CO)_5^-$ (M = Mn, Re), with $M_3(CO)_{12}$ (M = Fe, Ru, Os) leads to a wide mixture of products.[3]

$$Re(CO)_5^- + Os_3(CO)_{12} \rightarrow [\ ] \xrightarrow{H^+} H_3ReOs_3(CO)_{13} + HReOs_3(CO)_{15} + HReOs_2(CO)_{12} + HReOs_3(CO)_{16} \quad (2)$$

Similar reactions are observed for $Mn(CO)_5^-$ as anion or for $Ru_3(CO)_{12}$ as the cluster.[3] The reactions of $M_3(CO)_{12}$ with $Co(CO)_4^-$ have also been reported.[4]

$$Co(CO)_4^- + M_3(CO)_{12} \rightarrow \xrightarrow{H^+} HCoM_3(CO)_{13} \quad (3)$$

$$M = Ru, Os$$

$$Co(CO)_4^- + Fe_3(CO)_{12} \rightarrow \xrightarrow{H^+} HCo_3Fe(CO)_{12} + Co_4(CO)_{12} \quad (4)$$

The use of manganese carbonylate as a reducing agent (not incorporated in the product) has also been reported[5]

$$Ru_3(CO)_{12} \xrightarrow{Mn(CO)_5^-} \xrightarrow{H^+} HRu_6(CO)_{18}^- + H_3Ru_4(CO)_{12}^- \quad (5)$$

although a mixed-metal cluster may be an intermediate as in the formation of $Fe_6(CO)_{16}C^{-2}$ from $Fe(CO)_5$ and $Mn(CO)_5^-$. Alkali-metal reductions of $Ru_3(CO)_{12}$ have been reported to generate a variety of anions.[6] While reactions such as 1-9 have proven synthetically useful, there have been no kinetic or mechanistic studies of the reduction of cluster complexes.

As a continuation of our exploration of the mechanisms of reaction of metal carbonyl anions with various oxidizing agents,[7] we now report on the reactions of metal carbonyl

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