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Kinetics of dihydrogen activation by $Co_2Rh_2(CO)_{12}$ disproportionation and a second order cluster fragmentation *

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Abstract

The highly reactive mixed metal cluster $Co_2Rh_2(CO)_{12}$ has been shown to undergo selective disproportionation under hydrogen according to $3Co_2Rh_2(CO)_{12} \rightarrow 2Co_3Rh(CO)_{12} + Rh_4(CO)_{12}$. The reaction, which may be classified as an intermolecular redistribution reaction, was carried out in n-hexane at $T = 275$–294 K and $P_{H_2} = 0.4$–1.0 MPa and studied by use of high pressure *in situ* infrared spectroscopy. No reaction intermediates were observed. The reaction has an order of 1.0 ± 0.1 with respect to hydrogen and is second order in the metal carbonyl cluster $Co_2Rh_2(CO)_{12}$, it has an apparent activation energy E_a of 55 ± 8 kJ/mol (13 ± 2 kcal/mol). The low activation energy suggests that the rate-limiting step may not be the activation of molecular hydrogen. Furthermore, the second order dependence of the rate on the concentration of $Co_2Rh_2(CO)_{12}$ is very unusual for a cluster fragmentation reaction. Possible mechanisms giving rise to the observed kinetics are discussed.

Introduction

The mixed metal cluster $Co_2Rh_2(CO)_{12}$, which was first synthesized by Chini et al. [1], shows considerable reactivity in a wide variety of transformations. For example, it reacts with up to two equivalents of PEt_3 to give the simple substitution products $Co_2Rh_2(CO)_{11}PEt_3$ and $Co_2Rh_2(CO)_{10}(PEt_3)_2$, in which exclusive substitution at rhodium has occurred, but undergoes cluster fragmentation to $CoRh(CO)_5(PEt_3)_2$ when treated with four equivalents of PEt_3 [2]. $Co_2Rh_2(CO)_{12}$ also reacts with PhC_2Ph to give $Co_2Rh_2(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$ in which the Co–Co bond has been exclusively cleaved [3]. Pino et al. have shown that $Co_2Rh_2(CO)_{12}$ reacts with CO to give $CoRh(CO)_7$ [4], and that the tetranuclear and dinuclear carbonyls co-exist in an observable equilibrium ($\Delta_r G^\circ(293\ K) = -4.0$ kcal/mol) under low CO partial pressures [5]. Further, kinetic studies have shown that two

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* Dedicated by M.G. to the memory of Professor Piero Pino, who had approved the draft of this paper before his untimely death.

parallel reaction mechanisms are responsible for the fragmentation, as indicated by the rate constant $k_{obs} = \{k_1 + k_2[CO]\}$. The presence of the non-negligible term k_1 strongly suggests that spontaneous cleavage of a metal–metal bond in $Co_2Rh_2(CO)_{12}$ is one of the rate-determining steps [6]. The above reactions occur rapidly at ambient temperature.

The complex $Co_2Rh_2(CO)_{12}$ also shows considerable activity as a catalyst precursor at 298 K in both hydroformylation [7] and hydrogenation [8]. These results indicate that hydrogen activation readily occurs in these systems in either the presence or absence of CO. Furthermore, hydrogen activation studies carried out in the presence of CO have shown that the reaction involves the initial transformation of $Co_2Rh_2(CO)_{12}$ to $CoRh(CO)_7$ [9]. The coordinately unsaturated species $CoRh(CO)_7$ subsequently reacts with dihydrogen to generate $HCo(CO)_4$ and a transient species $\{HRh(CO)_3\}$, and the latter undergoes rapid conversion into $Rh_4(CO)_{12}$ [10].

In the absence of CO and the presence of hydrogen, $Co_2Rh_2(CO)_{12}$ disproportionates to $Co_3Rh(CO)_{12}$ and $Rh_4(CO)_{12}$ (eq. 1). The reaction, which can be classified as an intermolecular redistribution [11], was carried out in n-hexane solution and monitored by *in situ* infrared spectroscopy. Only ν(M–CO) vibrations from $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$ and $Rh_4(CO)_{12}$ were observed during the reactions. The reaction appears to be one of the first examples of an intermolecular redistribution process involving a metal–organic cluster in which there is exchange of central atoms rather than ligands. Intramolecular redistribution reactions involving the exchange of central atoms in cluster compounds, also known as "framework isomerism" have been reported [12]. In the present study, the dependence of the rate of reaction 1 on the concentrations $[Co_2Rh_2(CO)_{12}]$ and $[H_2]$ and on the temperature has been examined.

$$3Co_2Rh_2(CO)_{12} \xrightarrow{H_2} 2Co_3Rh(CO)_{12} + Rh_4(CO)_{12} \qquad (1)$$

Experimental

Chemicals

$Co_2Rh_2(CO)_{12}$ was prepared from $NaCo(CO)_4$ and $[Rh(CO)_2Cl]_2$ in n-hexane [4]. Elemental analysis (by courtesy of Ciba Geigy AG, Basel): 21.7% carbon (21.8% calculated), and 31.1% rhodium (31.2% calculated). Puriss-quality n-hexane from Fluka AG was refluxed over K/Na alloy under nitrogen. Nitrogen (99.999%) and hydrogen (99.999%) were purchased from Pan Gas AG (Luzern).

Equipment

A stirred autoclave connected to a high pressure infrared cell was used for all the kinetic experiments. The system was cooled with a Lauda RX20 cryostat (BRD). The n-hexane solution was pumped continuously from the autoclave to the high-pressure flow-through cell and back to the autoclave under isothermal ($\Delta T = 0.5\,^{\circ}C$) and isobaric conditions with a high-pressure membrane pump (Model DMK30, Orlita, BRD). A 1.000 MPa piezoelectric crystal was used for pressure measurements (Keller AG, Winterthur, Switzerland), and Pt-100 thermoresistors were used for temperature measurements in the autoclave, and the high-pressure cell.

A Perkin–Elmer PE983 infrared spectrophotometer was used for all quantitative measurements of the *in situ* metal carbonyl concentrations during the kinetic experiments. The PE983 was connected to a Model 3600G Data Station where the spectra were stored and then analyzed off-line.

Procedure

Typically, a solution of 33 mg $Co_2Rh_2(CO)_{12}$ in 200 ml of n-hexane (3.3×10^{-5} mol fraction) was transferred to the thermostated stirred autoclave and nitrogen was then introduced to give a total system pressure of 0.2 MPa. The solution in the autoclave was then pumped continuously from the autoclave to the high-pressure cell and back to the autoclave. At what was taken to be zero time, hydrogen was introduced into the autoclave to a selected partial pressure P_{H_2}, and at the same time a program to record repeated intensity measurements at $\nu = 1873$ cm^{-1} and to store this data at 20-s intervals was initiated. Additionally, complete spectra at 2200–1800 and at 1300–1100 cm^{-1} were taken at the start and end of the reaction. Little to no additional noise could be observed in the 2200–1800 or 1300–1100 cm^{-1} spectra when the solution was flowing with a typical velocity of 10 cm/s through the high-pressure cell. Experiments were carried out at hydrogen partial pressures P_{H_2} of 0.4, 0.6, 0.8 and 1.0 MPa at $T = 293$ K, and at temperatures T of 275, 282, 290 and 293 K with $P_{H_2} = 0.8$ MPa.

Calculations

The extinction coefficients for $Co_2Rh_2(CO)_{12}$ and n-hexane used in this study were $\epsilon(1873 \text{ cm}^{-1}) = 3640$ l mol^{-1} cm^{-1} and $\epsilon(1138 \text{ cm}^{-1}) = 2.353$ l mol^{-1} cm^{-1} [13]. The variation of the concentration of $Co_2Rh_2(CO)_{12}$ as a function of time, i.e. $[Co_2Rh_2(CO)_{12}]_t$, was expressed in terms of the dimensionless Beer–Lambert–Bouguer law, as indicated in eq. 2 [14], where the subscripts "tet" and "hex" refer to the tetranuclear complex and hexane, respectively.

$$x_{\text{tet}}(t) = \left(A_{\text{tet}}(t)\epsilon_{\text{hex}}\right)/\left(A_{\text{hex}}(t_0)\epsilon_{\text{tet}}\right) \qquad (2)$$

Henry's constant for the solubility of hydrogen in n-hexane was calculated from eq. 3, where P_{sat} is the saturated vapour pressure of the pure solvent [15]. Equation 3 was obtained by regression of literature data [16], and is consistent with the temperature dependence suggested by Jonah [17]. The Krichevsky–Kasarnovsky equation was not used to correct for the small change in the Henry constant due to total pressure effects in the interval 0.4–1.0 MPa [18].

$$\ln\left(H_{H_2}/P_{\text{sat}}\right) = -1.46 + 2840/T \qquad (3)$$

Results

Effect of hydrogen

Four experiments were carried out in order to determine the effect of hydrogen on the rate of disproportionation of $Co_2Rh_2(CO)_{12}$. At a time $t = 0$, hydrogen (0.4, 0.6, 0.8 and 1.0 MPa) was introduced into the thermostated stirred autoclave (293.2 K) containing 200 ml of a 3.3×10^{-5} mole fraction $Co_2Rh_2(CO)_{12}$ in n-hexane solution. The concentrations of $Co_2Rh_2(CO)_{12}$ during the first 2 h of reaction in these experiments are presented in Fig. 1. No change in the concentration of $Co_2Rh_2(CO)_{12}$ was observed before the addition of hydrogen.

Conversions of 50–60% were achieved in the four experiments in the first 2 h of reaction (Fig. 1). Quantitative conversion of $Co_2Rh_2(CO)_{12}$ into $Co_3Rh(CO)_{12}$ and $Rh_4(CO)_{12}$ was eventually observed in these experiments ($\Delta_r G^\circ < 0$), but reaction times of more than 12 h were typically required before the infrared absorbance attributed to $Co_2Rh_2(CO)_{12}$ at 1873 cm^{-1} was no longer detectable. Such a very long reaction compared with the first half-life of 2 h suggests that the cluster fragmentation is higher than first order in $[Co_2Rh_2(CO)_{12}]$.

If the transformation of the cluster $Co_2Rh_2(CO)_{12}$ is tentatively assumed to be second order with respect to the concentration of $Co_2Rh_2(CO)_{12}$ and nth order with respect to the concentration of dissolved hydrogen, the power law expression shown in eq. 4 can be written, and integrated to give eq. 5. Use of the rate constant $2k$ rather than k is consistent with the accepted notation [19]. A constant liquid phase hydrogen concentration for the duration of an experiment is implicit in these equations.

$$\mathrm{d}[Co_2Rh_2(CO)_{12}]/\mathrm{d}t = -2k[Co_2Rh_2(CO)_{12}]^2[H_2]^n \quad (4)$$

$$1/[Co_2Rh_2(CO)_{12}]_t - 1/[Co_2Rh_2(CO)_{12}]_o = 2k_{obs}t \quad (5)$$

The rate data from Fig. 1 were analyzed using eq. 5. As can be seen from Fig. 2, straight lines were obtained, confirming the second order dependence on $[Co_2Rh_2(CO)_{12}]$. The intercept at 3.1×10^4 mol fraction^{-1} corresponds to the initial concentration of metal carbonyl cluster. Deviations of the intercepts from 3.1×10^4 mol fraction^{-1} simply indicate a base line shift when hydrogen was added. In this respect, the quality of the data obtained at $P_{H_2} = 0.6$ MPa is poor.

The apparent rate constants $k_{obs}([H_2])$ were $k_{obs}(0.4\ \mathrm{MPa}) = 9.4 \times 10^{-2}$, $k_{obs}(0.6\ \mathrm{MPa}) = 2.9 \times 10^{-1}$, $k_{obs}(0.8\ \mathrm{MPa}) = 2.0 \times 10^{-1}$ and $k_{obs}(1.0\ \mathrm{MPa}) = 2.3 \times 10^{-1}$ (mole fraction)$^{-1}$ min^{-1}. If the data obtained at $P_{H_2} = 0.6$ MPa are omitted, the order in hydrogen is 1.0 ± 0.1.

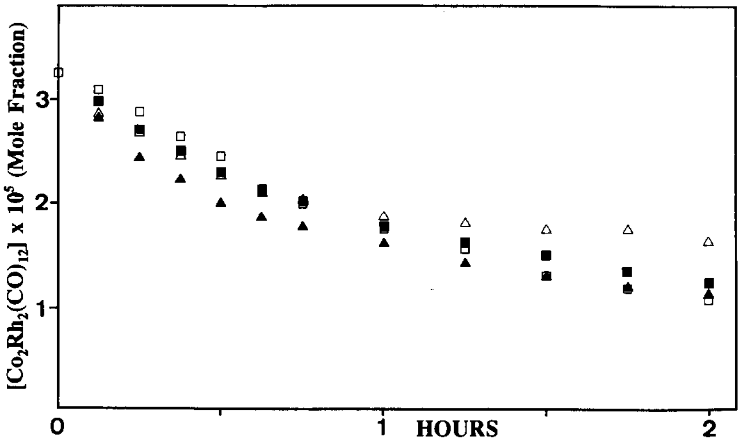

Fig. 1. Effect of hydrogen on the conversion of $Co_2Rh_2(CO)_{12}$. $[Co_2Rh_2(CO)_{12}]_o = 3.3 \times 10^{-5}$ mol fraction. Solvent: n-hexane. 0.2 MPa nitrogen, 293.2 K. △, 0.4 MPa; □, 0.6 MPa; ■, 0.8 MPa; ▲, 1.0 MPa.

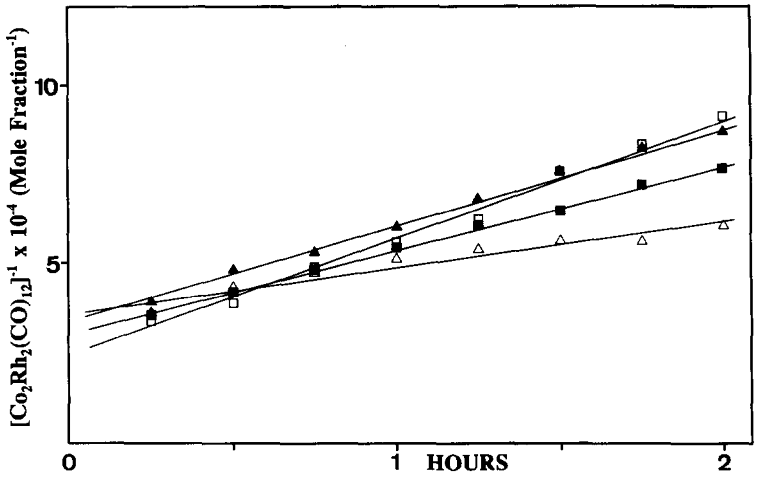

Fig. 2. Second-order disappearance of $Co_2Rh_2(CO)_{12}$. 0.2 MPa nitrogen, 293.2 K. △, 0.4 MPa; □, 0.6 MPa; ■, 0.8 MPa; ▲, 1.0 MPa.

Effect of temperature

Four experiments were carried out in order to determine the effect of temperature on the rate of the disproportionation reaction 1. At zero time and with a stirring speed of 200 RPM, 0.8 MPa hydrogen was introduced into the stirred autoclave containing a 3.3×10^{-5} mole fraction solution of $Co_2Rh_2(CO)_{12}$ in n-hexane and 0.2 MPa nitrogen. The decrease in the concentration of $Co_2Rh_2(CO)_{12}$ during the first 2 h of reaction in these experiments is presented in Fig. 3.

The rate constants $k_{obs}(T)$ were determined using eq. 5. The transformed data are shown in Fig. 4, and it can be seen that straight lines are again obtained. The data are considerably better than those shown in Fig. 2 for the hydrogen dependence of the rate of disproportionation. The intercepts for each experiment are

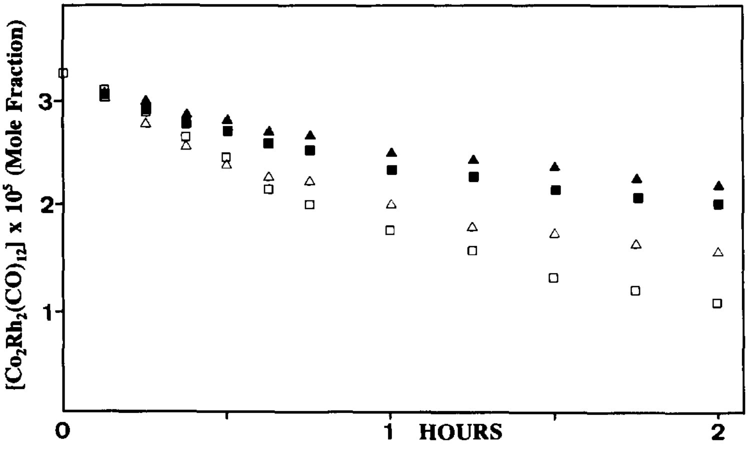

Fig. 3. Effect of temperature on the conversion of $Co_2Rh_2(CO)_{12}$. $[Co_2Rh_2(CO)_{12}]_o = 3.3 \times 10^{-5}$ mole fraction. Solvent: n-hexane. 0.2 MPa nitrogen, 0.8 MPa hydrogen. ▲, 275.5 K; ■, 282.2 K; △, 289.9 K; □, 293.2 K.

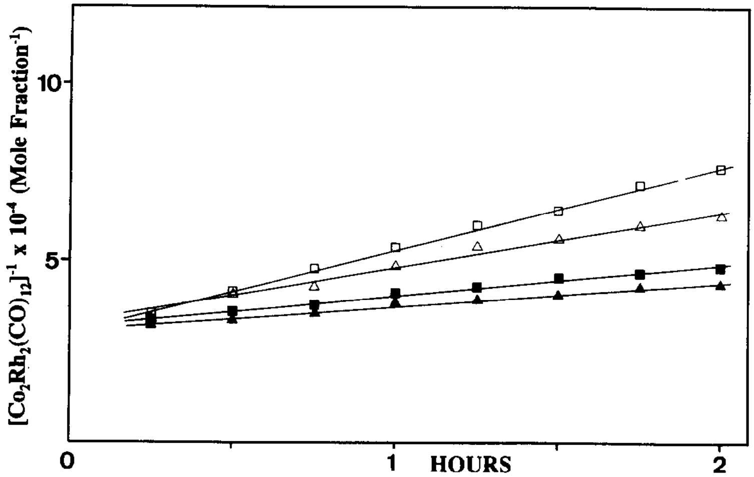

Fig. 4. Second-order disappearance of $Co_2Rh_2(CO)_{12}$. 0.2 MPa nitrogen. 0.8 MPa hydrogen. ▲, 275.5 K; ■, 282.2 K; △, 289.9 K; □, 293.2 K.

almost exactly 3.1×10^4 (mole fraction)$^{-1}$, and hence no significant baseline shifts occurred when hydrogen was added to the system. The experimentally determined values of $k_{obs}(T)$ were $k_{obs}(275.5\ K) = 5.7 \times 10^{-2}$, $k_{obs}(282.2\ K) = 7.3 \times 10^{-2}$, $k_{obs}(289.9\ K) = 1.3 \times 10^{-1}$ and $k_{obs}(293.2\ K) = 2.0 \times 10^{-1}$ (mole fraction)$^{-1}$. If the rate constants k are calculated from the expression $k_{obs} = k[H_2]$, where the concentration of dissolved hydrogen is expressed in mole fraction units, then the apparent activation energy, E_a, is 55 ± 8 kJ/mol (13 ± 2 kcal/mol).

In situ spectra

Figures 5, 6 and 7 show typical *in situ* spectra for the disproportionation reaction of $Co_2Rh_2(CO)_{12}$ under hydrogen. During the reaction only the complexes

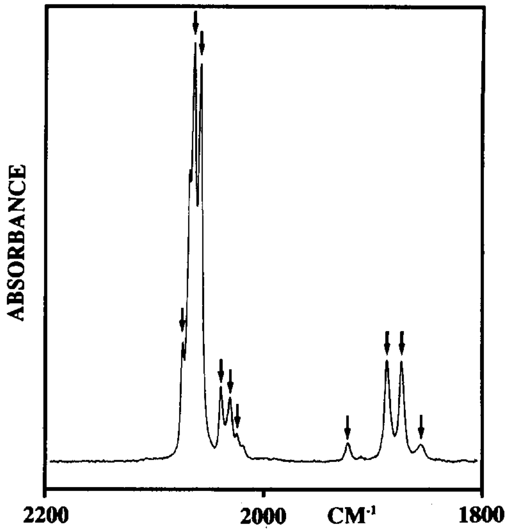

Fig. 5. *In situ* infrared spectrum of $Co_2Rh_2(CO)_{12}$ in n-hexane at 293 K under 0.2 MPa nitrogen.

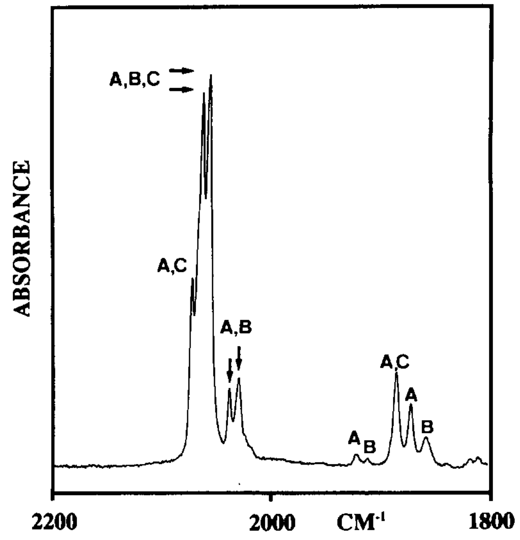

Fig. 6. *In situ* infrared spectrum 30 min after addition of 1.0 MPa hydrogen to $Co_2Rh_2(CO)_{12}$ in n-hexane at 293 K. A: $Co_2Rh_2(CO)_{12}$; B: $Co_3Rh(CO)_{12}$; C: $Rh_4(CO)_{12}$.

$Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$ and $Rh_4(CO)_{12}$ are observed, as indicated by the characteristic metal carbonyl infrared bands for $Co_2Rh_2(CO)_{12}$ at 2074, 2064, 2059, 2038, 2030, 1920, 1910, 1885, 1871, 1858 cm^{-1} [1], $Co_3Rh(CO)_{12}$ at 2066, 2059, 2056, 2037, 2031, 1909, 1882, 1856 cm^{-1} [1], and $Rh_4(CO)_{12}$ at 2074, 2068, 2061, 2043, 1885 cm^{-1} [20]. After 24 h, only the products $Co_3Rh(CO)_{12}$ and $Rh_4(CO)_{12}$ are observed. For comparison, the infrared absorbance maxima for $Co_4(CO)_{12}$ appear at 2110, 2058, 2030, 1996m, 1905, 1873vs, and 1838m cm^{-1} [21].

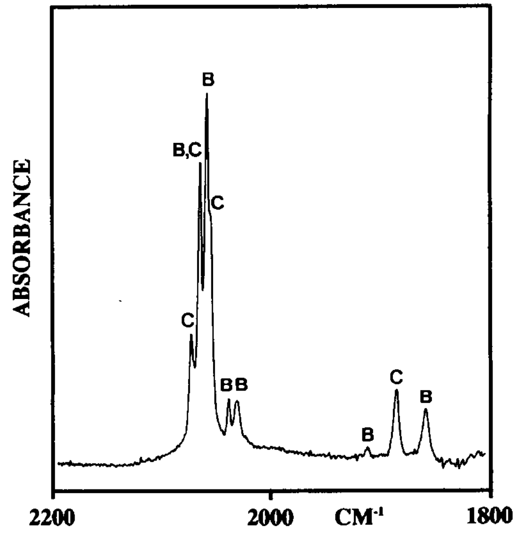

Fig. 7. *In situ* infrared spectrum 24 h after addition of 1.0 MPa hydrogen to $Co_2Rh_2(CO)_{12}$ in n-hexane at 293 K. A: $Co_2Rh_2(CO)_{12}$; B: $Co_3Rh(CO)_{12}$; C: $Rh_4(CO)_{12}$.

Discussion

The disproportionation of $Co_2Rh_2(CO)_{12}$ to $Co_3Rh(CO)_{12}$ and $Rh_4(CO)_{12}$ shows three principal characteristics; (i) a first-order dependence on the liquid phase concentration of hydrogen, (ii) a second-order dependence on $[Co_2Rh_2(CO)_{12}]$, and (iii) a relatively low activation energy, E_a, of 55 kJ/mol. Even though there is a first-order dependence on hydrogen, the relatively low activation energy suggests that reaction with molecular hydrogen may not be a rate-limiting step in the overall transformation under the conditions used. Indeed, since $Co_2Rh_2(CO)_{12}$ is coordinatively saturated, CO dissociation or M–M cleavage is almost certainly required before oxidative addition of hydrogen can occur, and hence a rather high apparent activation energy would be expected [10,22].

$$d[Co_2Rh_2(CO)_{12}]/dt = -2k_0 \exp(-E_a/RT)[Co_2Rh_2(CO)_{12}]^2[H_2]^{1.0} \qquad (6)$$

The second-order dependence on $[Co_2Rh_2(CO)_{12}]$ is very unusual. Indeed, the kinetics of virtually all cluster fragmentations which have been extensively studied to date conform to the general expression rate $= \{k_1 + k_2[L] + k_3[L]^2\}[\text{cluster}]^1$ (L = CO) where one or more terms in the summation are usually negligible [6,23]. In the above expression, it is the first-order dependence on the cluster concentration which is the most important aspect of the cluster fragmentation kinetics. Three explanations are suggested below to account for the reaction orders observed for reaction (1). Two involve mechanisms emphasizing the fragmentation kinetics of the cluster $Co_2Rh_2(CO)_{12}$, and the other mechanism focuses on the recombination kinetics.

One simple reaction scheme (eqs. 7a and 7b) consistent with the kinetic observations involves the initial formation of a species of stoichiometry $\{H_2Co_2Rh_2(CO)_x\}$ followed by a bimolecular interaction of this species with $Co_2Rh_2(CO)_{12}$. Though consistent with the kinetic data, eqs. 7a and 7b do not provide a very satisfactory explanation for the high reactivity of $Co_2Rh_2(CO)_{12}$,

$$H_2 + Co_2Rh_2(CO)_{12} \rightleftharpoons \{H_2Co_2Rh_2(CO)_x\} + (12-x)CO \qquad (7a)$$

$$\{H_2Co_2Rh_2(CO)_x\} + Co_2Rh_2(CO)_{12} \rightarrow \ldots \qquad (7b)$$

A second possible mechanism which might account for the observed kinetics, involves the initial bimolecular encounter of two clusters to yield a highly reactive or "activated" cluster, denoted by $Co_2Rh_2(CO)_x^\star$, followed by its reaction with hydrogen. Such a bimolecular reaction, of Type 1 (see ref. 24), occurs rarely and then almost exclusively in the gas phase, where sufficient kinetic energy is available to generate an excited intermediate. Furthermore, this mechanism also seems somewhat unlikely because $Co_2Rh_2(CO)_{12}$ undergoes a very rapid unimolecular activation in solution, as indicated by the significant first-order term $k_1[Co_2Rh_2(CO)_{12}]$ observed during the fragmentation to $CoRh(CO)_7$ [6].

$$Co_2Rh_2(CO)_{12} + Co_2Rh_2(CO)_{12} \rightarrow Co_2Rh_2(CO)_x^\star + Co_2Rh_2(CO)_{12} + (12-x)CO \qquad (8)$$

Finally, the reaction of $Co_2Rh_2(CO)_{12}$ with hydrogen to give numerous lower nuclearity metal carbonyl hydrides and metal carbonyls could in fact be very rapid, and so recombination of these lower-nuclearity species might determine the observed kinetics. Indeed, this concept is very similar to that of "stepwise complex formation", a process previously invoked for some redistribution reactions [11a]. Such recombination mechanisms belong to the broad category of consecutive reactions, for which the mathematical treatment of the "uniform flux approximation" and so called "kinetically significant sequences" have been worked out [26]. In the present reaction, two sequences can be written for the overall reaction, namely (i) $Co_2Rh_2(CO)_{12} \rightleftharpoons$ [intermediates] $\rightarrow Co_3Rh(CO)_{12}$ and (ii) $Co_2Rh_2(CO)_{12} \rightleftharpoons$ [intermediates] $\rightarrow Rh_4(CO)_{12}$, where either sequence could be kinetically significant. For example, if one considers the hypothetical reaction scheme $2Co_2Rh_2(CO)_{12} + H_2 \rightleftharpoons 2\{HRh_2(CO)_6\} \ldots \rightarrow Rh_4(CO)_{12} + H_2$, it appears possible to obtain a rate expression proportional to $[Co_2Rh_2(CO)_{12}]^2$ and $[H_2]$, but there are other complications.

In conclusion, the mixed metal cluster $Co_2Rh_2(CO)_{12}$ has been shown to disproportionate under hydrogen with the unusual dependence of the rate on $[Co_2Rh_2(CO)_{12}]^2$. Even though the origin of the reaction orders could not be identified, the existence of lower nuclearity metal carbonyl hydrides in the system seems reasonable, and would help to account for the activity of this cluster as a catalyst precursor in hydrogenation.

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