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(23) As detailed in the Experimental Section no correction was made for the warm-up time, i.e., the time required before the reaction mixture attained the bath temperature. The extrapolated abscissa intercept of Figure 1 would indicate warm-up times of the order of 5 min.

(24) R. Nishiguchi and K. Fukuzumi report[6] that, with $RhCl(PPh_3)_3$ as the catalyst, the transfer-hydrogenation reaction is zero-order in cyclopentene. We have been unable to reproduce this result.

(25) Nishiguchi et al. report that in the region where the catalyst concentration is higher than 0.003 M the rate might be regarded as having pseudo-first-order dependence on the catalyst concentration.

(26) T. Nishiguchi and K. Fukuzumi state[6] that, whereas toluene is a suitable cosolvent, benzene strongly inhibits the transfer-hydrogenation reaction. We have been *unable* to *reproduce* this surprising result; in fact, we found that addition of 0.5 M benzene to the reaction mixture (reported[6] to depress the rate of reduction of cyclopentene to ca. one-eighth) had little effect on the reaction rate: k_{obsd} (absence of benzene) $= 2.4 \pm 0.2\ 10^{-4}\ s^{-1}$; k_{obsd} (addition of 0.5 M benzene) $= 2.1 \pm 0.2 \times 10^{-4}\ s^{-1}$.

(27) T. Nishiguchi and K. Fukuzumi report[6] a value of 21.6 kcal mol^{-1} (no error quoted).

(28) Using diphenylethylphosphine in place of triethylphosphine in the catalyst system we obtain a value of 2.9 ± 0.5 for the kinetic isotope effect at 180 °C. Nishiguchi et al.[6] report a value of 3.1 with $RhCl(PPh_3)_3$ as the catalyst.

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(38) Analogous kinetic behavior has been observed by Zajacek et al.[40] in the molybdenum-catalyzed epoxidation of 1-octene by organic hydroperoxides.

(39) An alternative scheme, viz.

$$\begin{gathered} D + M \rightleftharpoons MD \\ MD + C \rightleftharpoons MDC \\ MD + P \rightleftharpoons MDP \\ MDC \rightarrow M + P + CH_2 \end{gathered}$$

involving prior coordination of dioxane to the catalytic species would, clearly, give the same kinetic results.

(40) T. N. Baker, G. J. Mains, M. N. Sheng, and J. G. Zajacek, *J. Org. Chem.*, **38**, 1145 (1973).

(41) An analogous treatment of the data presented in Table VIII also provides, in principle, a method of obtaining a value of K_p, i.e., a plot of ${k_{obsd}}^{-1}$ vs. $[C]_0 + [P]_0$ being linear (see Figure 3, ${k_{obsd}}^{-1}$ vs. $[P]_0$) and division of the slope by the intercept giving K_p. However, although in this case both intercepts are positive, 504 ± 206 and 205 ± 373 for catalysts A and B, respectively, the errors involved preclude a meaningful value of K_p being obtained. Qualitatively the discussion is similar to that of the $Rh_2Cl_2(cyclooctene)_4$–$4PEt_3$ data shown in Figure 2.

(42) No such difficulty was encountered with the $Rh_2Cl_2(cyclooctene)_4$–$4PEt_3$ system.

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The Catalytic Reduction of Nitric Oxide by Carbon Monoxide Using Dichlorodicarbonylrhodium(I) Anion

Carol D. Meyer and Richard Eisenberg*

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627.

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Abstract: The catalytic reduction of nitric oxide by carbon monoxide to yield N_2O and CO_2 has been studied at 23°C using $[RhCl_2(CO)_2]^-$ as the catalyst. When solutions of the rhodium carbonyl anion in aqueous acidic ethanol are placed under a mixed gas atmosphere of NO and CO (4:3 ratio), a green color develops characteristic of an unstable intermediate and product evolution is observed by GC analysis. Quantitative recovery of $[RhCl_2(CO)_2]^-$ at the end of the catalytic runs and recharging of the rhodium carbonyl anion solutions with no loss of activity indicate the true catalytic behavior of this system. It is also found that H_3O^+ is a necessary cocatalyst for this reaction. The green catalytic intermediate is proposed as a dinitrosylcarbonyl and a mechanism for the catalytic cycle is presented. Studies using $RhCl_3$ solutions establish that reduction of Rh(III) to $[RhCl_2(CO)_2]^-$ is a necessary prerequisite to the onset of catalytic activity under NO/CO atmospheres.

The catalytic reduction of nitric oxide by carbon monoxide possesses both intrinsic interest and environmental importance. The former arises from the extensive bond reorganizations implicit in reactions 1 and 2 including the oxygen atom transfers required by their stoichiometries.

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad (1)$$

$$2NO + CO \rightarrow N_2O + CO_2 \quad (2)$$

The environmental importance results from the presence of both NO and CO in most combustion exhausts and the need to convert these compounds into less harmful chemical entities.

While reactions 1 and 2 are overwhelmingly favored thermodynamically, they do not proceed at appreciable rates in the absence of a catalyst. To date, most studies of the catalyzed reduction of nitric oxide by carbon monoxide have employed heterogeneous catalysts, usually metals and metal oxides, at elevated reaction temperatures.[1] The use of metal complexes in solution as catalysts for reactions of this type has only recently begun to be explored. In 1973 Johnson and Bhaduri[2] reported that the dinitrosyl $[Ir(NO)_2(PPh_3)_2]^+$ reacts with carbon monoxide according to eq 3, and conversion of the cationic tricarbonyl complex $[Ir(CO)_3(PPh_3)_2]^+$ back to the reactant dinitrosyl suggested the possibility of a continuous cycle for reaction 2. Catalysis of eq 2 by such dinitrosyl complexes has subsequently been reported by Haymore and Ibers.[3]

$$Ir(NO)_2L_2^+ + 4CO \rightarrow Ir(CO)_3L_2^+ + N_2O + CO_2 \quad (3)$$

In our laboratory studies were initiated using metal complexes in solution under gaseous mixtures of NO and CO, and indeed catalysis of reaction 2 was observed with $RhCl_3$ in ethanol.[4] In retrospect, this catalysis derives logically from the report by Hughes[5] on the reaction of NO with Rh(I) systems according to eq 4 and the known CO reduction of $RhCl_3$, reaction 5, as reported by James and coworkers.[6] In the former the Rh(I) metal center is apparently oxidized to Rh(III) with the production of N_2O, whereas in the latter the metal center is reduced to Rh(I) and CO_2 is evolved. Coupling of (4) and (5) thus predicts the observed catalysis.

$$RhClL_2L' + 4NO \rightarrow RhCl(NO_2)(NO)L_2 + L' + N_2O \quad (4)$$

$$RhCl_3 + 3CO + H_2O \rightarrow [RhCl_2(CO)_2]^- + CO_2 + 2H^+ + Cl^- \quad (5)$$

In the present paper we describe a comprehensive development of our initial observations[4] including identification of $[RhCl_2(CO)_2]^-$ as the true catalyst in this system, the need for aqueous acid as a cocatalyst, and a discussion of the mechanistic possibilities of this intriguing reaction.

Experimental Section

General Methods and Materials. Rhodium trichloride hydrate (Matthey Bishop), tetraphenylarsonium chloride (Ventron), and triphenylphosphine (Eastman) were used as purchased. Nitric oxide was purified by passage through a cold trap (−78°C). Carbon monoxide was used directly. Both gases were obtained from Matheson. Reagent grade solvents were dried and distilled under nitrogen just prior to use. Concentrated HCl refers to a 37% aqueous solution.

A Hewlett-Packard Series 5700A gas chromatograph with a thermal conductivity detector was used for analysis of gas mixtures. Gas samples (0.50 ml) were taken with a Pressure-Lok air tight gas syringe (Series A-2) obtained from Precision Sampling Corporation. Separation of diatomic gases (N_2, O_2, CO, and NO) was achieved on a Molecular Sieve 5A column (2 ft × 0.5 in.), and a Porapak Q column (12 ft × 0.25 in.) was employed for separation of CO_2 and N_2O distinct from the diatomic gases. Both stainless steel columns were purchased prepacked from Hewlett-Packard.

The apparatus employed in the catalytic studies consisted of either a 1-l. (kinetic studies) or a 3-l. 24/40 single-neck round-bottom flask connected via a side arm to a three-way stopcock. One lead was connected to vacuum and the other used for addition of gases or stoppered with a serum cap to allow gas sampling. A ground glass adapter connected the reaction vessel to a mercury manometer. Solutions were stirred using a magnetic stirrer.

Isolation of products at the end of catalysis runs was achieved by transferring the final degassed solutions under vacuum and concentrating either under vacuum or under a stream of nitrogen. In trapping experiments triphenylphosphine (3 equiv) was injected as a concentrated solution in ethanol.

Infrared spectra were recorded (KBr pellets) on a Perkin-Elmer 467 grating infrared spectrophotometer. Ultraviolet and visible spectra were recorded on a Cary 118 spectrophotometer. A Beckman pyrocell (no. 5011) quartz flow cell was connected with narrow Tygon tubing to the reaction vessel sample port and to a 100-ml gas reservoir bulb attached to a mercury manometer. This sampling assembly was then evacuated and slowly filled with the gas mixture over the catalyst solution to a pressure differential of ca. 100 mm. The reaction vessel was then tilted, allowing the solution to flow into the sample cell. Hoffman clamps were used to seal the two Tygon leads.

Preparation of Complexes. The dimer $[Rh(CO)_2Cl]_2$ was prepared by the method of McCleverty,[7] recrystallized from hexane, and stored in a desiccator. The method of Cleare and Griffith[8] was used for the synthesis of $(AsPh_4)[RhCl_2(CO)_2]$.

Calibration Plots. A 1-l. reaction vessel connected to a mercury manometer was evacuated and flushed with gas (NO, CO, N_2O, or CO_2) several times. The desired gas was then added in small increments. System pressure was recorded and a 0.50-ml gas sample analyzed by GC after each addition. The gas pressure was taken as the difference between the vacuum pressure reading and the system pressure reading for a given sample. Linear plots of peak height vs. partial pressure were obtained for all four gases, and slopes were determined by a computer fitted least-squares analysis. New calibration plots were prepared whenever it became necessary to change the helium tank.

Catalysis Runs (I–XII). One millimole of $RhCl_3 \cdot xH_2O$, 1 mmol of $(AsPh_4)[RhCl_2(CO)_2]$, or 0.50 mmol of $[Rh(CO)_2Cl]_2$ was dissolved in 100 ml of absolute ethanol in the 3-l. reaction vessel, and additional reagents were added as noted in Tables I and II. The entire system was then thoroughly degassed and allowed to equilibrate to room temperature (0.5 hr). Carbon monoxide (ca. 260 mm) and nitric oxide (ca. 360 mm) were then added in that order, and the system was sampled immediately to give t_0 partial pressures of reactant gases.

Kinetic Runs (A–I). The complex $(AsPh_4)[RhCl_2(CO)_2]$ was weighed into a 100-ml volumetric flask and diluted to the mark with a stock solution prepared by adding 20 ml of concentrated hydrochloric acid to 500 ml of absolute ethanol. The solution was then poured into the 1-l. reaction bulb, attached to the manometer, cooled to −78°C, and degassed. Carbon monoxide was added, the solution thawed, cooled, and then evacuated. The entire freeze-pump-thaw cycle was then repeated, and the final degassed solution allowed to equilibrate to room temperature for at least 1 hr prior to charging with CO and NO successively. The system was sampled immediately to give t_0 values for partial pressures of reactant gases.

Results

Homogeneous catalysis of the reduction of nitric oxide by carbon monoxide was monitored by periodic sampling of gas mixtures above the rhodium complex solutions. The samples were analyzed by gas chromatography; from linear calibration plots of peak height vs. partial pressure for the pure gases, the partial pressures of reactant and product gases during the course of each run were calculated. In a control experiment no reaction was observed in the absence of rhodium complex.

The Catalyst Complex. Experimental results designed to determine the nature of the catalyst complex in the system first reported by Reed and Eisenberg[4] are presented in Table I. Curves of N_2O production as a function of time for key runs in the table are depicted in Figure 1. Analogous curves for CO_2 evolution were also obtained.

Each run commenced with an approximate 4:3 ratio of NO:CO unless otherwise noted. Since the stoichiometry of the catalyzed reaction conformed to eq 2, the NO:CO *ratio* of gases above the catalyst solution exhibited a continuous decrease. Run I using $RhCl_3 \cdot xH_2O$ in ethanol essentially duplicates the results reported previously by us.[4] Initially it was discovered that addition of a few milliliters of concentrated hydrochloric acid (run II) to the $RhCl_3 \cdot xH_2O$ solutions caused a twofold increase in product formation. In comparison to curve I, curve II clearly shows that the induction period is shortened and the maximum rate of product evolution increased in the aqueous acidic medium. Identical effects were observed in run III by stirring the $RhCl_3 \cdot xH_2O$ solution under carbon monoxide for several hours prior to degassing and charging with NO and CO. These results are indicative of initial reduction of Rh(III) to Rh(I) by carbon monoxide to give $[RhCl_2(CO)_2]^-$,[6] and it was found that this anion could be isolated as its tetraphenylarsonium salt by the addition of tetraphenylarsonium chloride to the final degassed solutions. Consequently, attention focused on the catalytic properties of this complex.

In runs IV and VI it was established that $[RhCl_2(CO)_2]^-$, whether produced by the addition of aqueous HCl to solutions of the chloro-bridged dimer[9] or introduced upon dissolution of an authentic salt in the same medium,[4] forms a reactive homogeneous catalyst system for

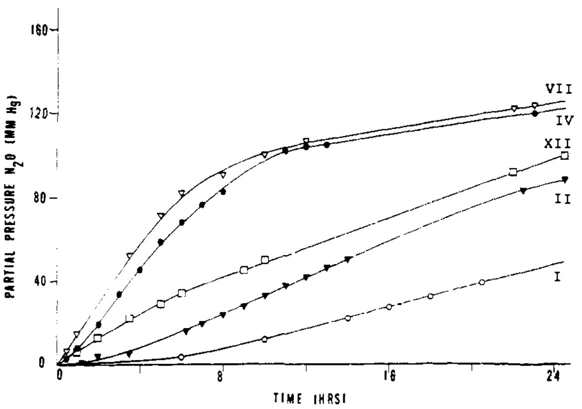


Figure 1. Partial pressure of N_2O vs. time for solutions of $(AsPh_4)[Rh(CO)_2Cl_2]$ and $RhCl_3{\cdot}xH_2O$. Roman numerals refer to runs listed in Tables I and II.

Table I. Homogeneous Catalysis of Nitric Oxide Reduction by Carbon Monoxide

Run	Catalyst solution[a]	Time (hr)	ΔP_{NO}[b]	ΔP_{CO}	P_{CO_2}	P_{N_2O}
I	$RhCl_3{\cdot}xH_2O$	20.5	110	66	52	39
II	$RhCl_3{\cdot}xH_2O$, 4 ml of HCl	23	270	158	111	83
III	$RhCl_3{\cdot}xH_2O$, 4 ml of HCl (treacted first with CO)	23	296	175	126	102
IV	$[Rh(CO)_2(\mu\text{-}Cl)]_2$, 4 ml of HCl	23	316	149	138	120
V	Recharge of run IV	23	304	143	145	125
VI	$Ph_4As[Rh(CO)_2Cl_2]$, 4 ml of HCl	23	314	149	138	128
VII	$Ph_4As[Rh(CO)_2Cl_2]$, 4 ml of HCl (treated first with NO)	23	342	204	142	124
VIII	$[Rh(CO)_2(\mu\text{-}Cl)]_2$, 4 ml of HCl (NO:CO = 2:1)	23	428	206	200	180

[a] All solutions contained 1 mmol of Rh in 100 ml of ethanol; other components are specified. Unless otherwise stated initial ratio of NO:CO was 4:3. HCl refers to a 37% aqueous solution. [b] Partial pressures are in millimeters of Hg. ΔP is initial partial pressure minus that at time shown. P is partial pressure of product at the end of the time period. Estimated errors are ±2%.

converting nitric oxide and carbon monoxide into N_2O and CO_2. The product curves for these runs (Figure 1) show a dramatically shortened induction period relative to the rhodium trichloride system. Solutions of the anion undergo a color change from pale yellow to olive green under an NO/CO atmosphere, producing within 1 hr a solution which is identical in appearance with those formed from ethanolic $RhCl_3{\cdot}xH_2O$ solutions after 8-10 hr exposure to the mixed gases. Product evolution continues at a fairly uniform rate during the ensuing 7 hr, and approximately 50% of the reactant gases, corresponding to the production of 15 mol of CO_2 and N_2O per mole of rhodium, are consumed within the first 8 hr. At this point the reaction rate begins to decrease rapidly, and the solution gradually changes color back to pale yellow, suggesting regeneration of the carbonyl anion as the CO:NO ratio of reactant gases above the solution increases.

Virtually quantitative recovery of $(AsPh_4)[RhCl_2(CO)_2]$ was achieved at the end of run VI. Alternatively, the final yellow solutions could be degassed and recharged repeatedly (run V), reproducing the results of the initial charge without any apparent loss of catalytic activity. This quantitative interconversion of $[RhCl_2(CO)_2]^-$ and the green catalytic intermediate was verified spectrophotometrically as outlined below.

Except possibly for ligand exchange, $[RhCl_2(CO)_2]^-$ does not react with carbon monoxide under the conditions of these experiments, leading to the conclusion that initial reaction involves either NO substitution or adduct formation. Consequently, the reaction of the carbonyl anion with nitric oxide alone was investigated, employing solutions identical with those used in run VI. Under an initial partial pressure of 360 mm NO solutions of $[RhCl_2(CO)_2]^-$ rapidly turned dark reddish orange. Gas chromatographic analysis established that stoichiometric evolution of 2 equiv of CO_2 and N_2O within 2 hr was followed by continued slow formation of nitrous oxide. The stoichiometry of nitric oxide consumption and product evolution suggested initial occurrence of reaction 6.

$$[RhCl_2(CO)_2]^- + 6NO \rightarrow [RhCl_2(NO)_2]^- + 2N_2O + 2CO_2 \quad (6)$$

Evacuation of the system and concentration of the solution afforded a dark red solid, which was only slightly soluble in most organic solvents. The infrared spectrum of this material had bands arising from the tetraphenylarsonium ion, a metal chlorine stretch at 330 cm^{-1}, and a broad unresolved absorption centered at 1620 cm^{-1} which was assigned to ν_{NO}. Attempts to obtain crystals suitable for further study were unsuccessful. The nature of the species formulated as $[RhCl_2(NO)_2]^-$ thus remains unestablished and its degree of solvation will be intimately related to the Rh oxidation state and nitrosyl bonding modes. The apparent continued disproportionation of nitric oxide catalyzed by these solutions is probably related to the observations of Stanko and co-workers,[10] although no attempt was made to isolate ethyl nitrite from the reaction mixture.

Evacuation of the system followed by reaction of the red solution with carbon monoxide resulted in evolution of CO_2 and N_2O and in the re-formation of $[RhCl_2(CO)_2]^-$, which was isolated in good yield from the final yellow solutions. Alternatively, if the solutions formed under NO were degassed and recharged with CO and NO in a 3:4 ratio, run VII (Figure 1) was obtained. The characteristic green color of the catalytic intermediate developed very rapidly, and onset of significant product formation occurred immediately. These results strongly suggest that interconversion between the red nitrosyl species, the green catalytic intermediate, and the carbonyl chloride anion is facile. The equilibrium between the latter two species is observed directly, as shown in Figure 2, by charging dilute solutions of the red nitrosyl complex under a CO atmosphere and sampling in a flow cell. The initial spectrum observed is that of the green catalytic intermediate, and during the following 2 hr, a gradual increase in the absorbance at 332.5 nm characteristic of $[RhCl_2(CO)_2]^-$ occurs along with a decrease in the higher wavelength absorbance of the intermediate and an isosbestic point at 360 nm. Dilute solutions of the carbonyl anion under a nitric oxide atmosphere exhibit very intense absorptions below 320 nm and well-defined shoulders at 390, 370, 356, 342, and 332 nm characteristic of the red nitrosyl species. All transitions had extinction coefficients greater than that of the carbonyl anion maximum and the large molar absorptivity of this complex in the region 320-400 nm (where the green intermediate absorbs weakly) precluded spectrophotometric observation of the conversion of the red nitrosyl species to the catalytic intermediate.

Effect of Aqueous Acid. While the shortened induction period resulting from addition of a few milliliters of hydrochloric acid to the rhodium trichloride system was antici-

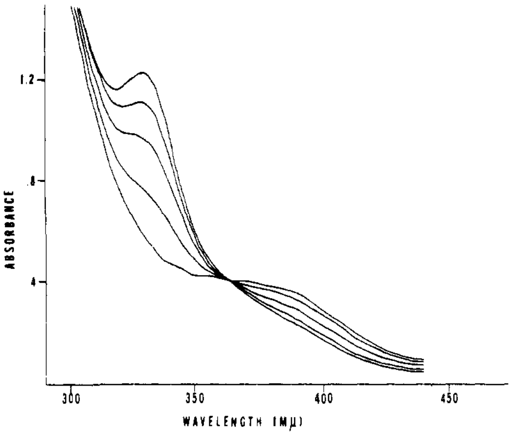


Figure 2. Ultraviolet absorption spectrum of the (AsPh$_4$)[Rh(CO)$_2$Cl$_2$] + NO product upon reaction with CO. An 0.628 m*M* solution of [Rh(CO)$_2$Cl$_2$]$^-$ in EtOH-HCl was stirred under NO for 3 hr, degassed, charged with CO, and immediately sealed in a flow cell. The spectrum was scanned at *t* = 5, 65, 80, 110, and 120 min. The [Rh(CO)$_2$Cl$_2$]$^-$ peak at 332.5 mμ (ϵ = 3.06 × 10^3 l./(*M* cm)) is unobserved at *t* = 5 min and grows throughout the time period.

Table II. Requirement for Acid and Water in the [Rh(CO)$_2$Cl$_2$]$^-$ Homogeneous Catalyst System

Run	Catalyst solution[a]	Time (hr)	ΔP_{NO}[b]	ΔP_{CO}	P_{CO_2}	P_{N_2O}
VI	Ph$_4$As[Rh(CO)$_2$Cl$_2$], 4 ml of HCl	23	314	149	138	128
IX	[Rh(CO)$_2$(μ-Cl)]$_2$, 1 ml of HCl	23	280	136	142	122
X	Ph$_4$As[Rh(CO)$_2$Cl$_2$], anhydrous	23	47	33	9	14
XI	Ph$_4$As[Rh(CO)$_2$Cl$_2$], ~40 mmol of HCl gas	21.5	46	16	9	5
XII	Ph$_4$As[Rh(CO)$_2$Cl$_2$], 3 ml of H$_2$O	23	243	100	98	91
XIII	Ph$_4$As[Rh(CO)$_2$Cl$_2$], 1.8 ml of H$_2$O, 1.4 g of LiCl	23	167	79	80	71
XIV	Ph$_4$As[Rh(CO)$_2$Cl$_2$], 6.3 ml of 70% HClO$_4$	24	262	129	139	117

[a] All solutions contained 1 mmol of Rh in 100 ml of ethanol; amounts of other components are specified. The initial ratio of NO:CO was 4:3. HCl in run IX was 37% aqueous. [b] Partial pressures are in millimeters of Hg. ΔP is the change in partial pressure of reactant gases from time zero to the time shown. *P* is the partial pressure of product gases at the end of the time period. Estimated errors are ±2% of reported values.

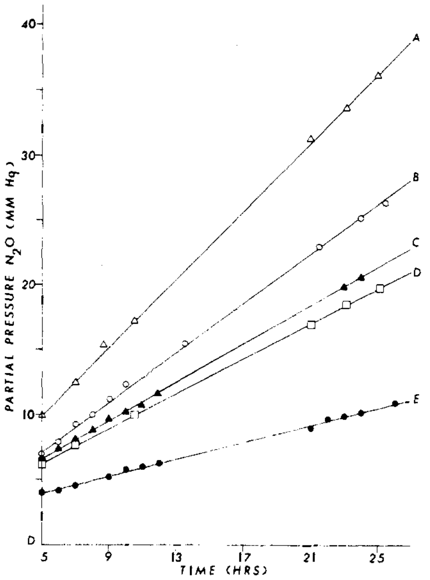


Figure 3. Dependence of the rate of N$_2$O production on initial (AsPh$_4$)[Rh(CO)$_2$Cl$_2$] concentration. Letters refer to runs listed in Table III.

Table III. Rate of Product Formation as a Function of Initial Metal Ion Concentration

Run	[Rh(CO)$_2$Cl$_2$]^-_i, × 10^4 *M*	ΔP_{N_2O}/hr (mm of Hg/hr)	ΔP_{CO_2}/hr (mm of Hg/hr)
A	5.871	1.31 ± 0.01	1.66 ± 0.02
B	4.403	0.98 ± 0.01	1.23 ± 0.01
C	3.995	0.74 ± 0.01	0.90 ± 0.02
D	2.935	0.68 ± 0.01	0.86 ± 0.01
E	1.631	0.33 ± 0.01	0.42 ± 0.01

pated, the enhanced *rate* of product formation in run II was not. This observation, along with the presence of aqueous HCl in the runs involving [RhCl$_2$(CO)$_2$]$^-$, prompted an investigation of the role of acid and water in the catalytic process. The results of these experiments are summarized in Table II. While decreasing both the concentration of water and acid by a factor of four (run IX) had no effect on the catalytic activity, only a very slow stoichiometric reaction was observed in strictly anhydrous medium, whether neutral (run X) or acidic (run XI). Conversely, addition of water alone (run XII) is sufficient to render the ethanolic solutions catalytically active, although the characteristic green color does not develop. As seen in curve XII (Figure 1), the maximum rate of product evolution is also significantly slower. In run XIII it was found that the effect of added chloride ion was negligible, and under conditions of approximately equal acidity (runs VI and XIV) the catalytic activity was not affected by substitution of the noncoordinating perchlorate counterion. Thus it became apparent that aqueous acid was required for maximum catalytic activity.

Kinetic Studies. Kinetic studies were undertaken in order to establish the rate dependence on both catalyst concentration and partial pressures of reactant gases. These experiments were conducted using more dilute solutions of [RhCl$_2$(CO)$_2$]$^-$ which prolonged the linear period of product evolution and facilitated accurate rate determinations. Linearity in the rate of product evolution over a 20-hr time interval was achieved by employing solutions with initial anion concentrations in the range 5.9 × 10^{-4} to 1.6 × 10^{-4} *M*, and slopes of these lines were determined by a computer least-squares analysis. The rates for N$_2$O and CO$_2$ production are presented in Table III and Figure 3.[11] Plots of log ($\Delta P_{N_2O}/\Delta t$) or log ($\Delta P_{CO_2}/\Delta t$) vs. log ([RhCl$_2$(CO)$_2$]$_i^-$ were linear with slopes of 1.02 ± 0.13 and 1.03 ± 0.12, respectively, establishing first-order dependence on metal ion concentration ([RhCl$_2$(CO)$_2$]$_i$ = initial anion concentration). Quantitative conversion of [RhCl$_2$(CO)$_2$]$^-$ to the catalytic intermediate within the first 5 hr of reaction was verified spectroscopically in a separate experiment. It should be noted that extrapolation of these results to runs IV and VI shows that the rates in the more concentrated solutions are slower than would be expected, indicating that the method of stirring may be insufficient to eliminate rate retardation arising from gas-liquid mass transfer effects. However, no systematic study has been made to date of the rate of product evolution as a function either of stirring or of gas-solution interface.

Semiquantitative kinetic studies designed to ascertain the importance of gas concentrations were also conducted with

Table IV. Rate of Product Formation as a Function of Initial Partial Pressures of Reactant Gases[a]

Run	$[Rh(CO)_2Cl_2]^-{}_i$, $\times 10^4$ M	$P_{NO}{}^i$ (mm of Hg)	$P_{CO}{}^i$ (mm of Hg)	Ratio^i NO/CO	ΔP_{N_2O}/hr (mm of Hg/hr)	ΔP_{CO_2}/hr (mm of Hg/hr)
F	2.981	261	208	1.25	0.63	0.72
G	2.981	207	167	1.24	0.57	0.64
H	2.935	406	211	1.92	0.55	0.66
I	2.935	213	394	0.54	1.19	1.28
D	2.935	374	278	1.35	0.68	0.86

[a] The symbol "i" refers to initial concentration, partial pressure, or ratio.

dilute solutions, and once again linear plots of product evolution vs. time were obtained. The slopes of these lines, determined by least-squares analysis, along with initial partial pressures of reactant gases are reported in Table IV. In run H (compare to run F) it was found that doubling the initial partial pressure of nitric oxide while keeping that of carbon monoxide constant had little effect on the rate of product formation. In marked contrast, comparison of run G and run I revealed a twofold rate enhancement observed upon doubling the initial partial pressure of carbon monoxide while holding that of nitric oxide constant. The similarity in rates for runs F, G, H, and D and the result for run I lead to the conclusion that the rate of product formation is strongly dependent only on the concentration of carbon monoxide.

The results of these experiments (and in particular run H) were quite surprising in light of seemingly opposite effects observed when 10^{-2} M solutions of $[RhCl_2(CO)_2]^-$ were charged initially with 420 mm of NO and 210 mm of CO (run VIII). It was anticipated that under conditions of a 2:1 (NO:CO) charge the rate of product evolution would have remained constant for a longer time period than it had under an initial 4:3 (NO:CO) charge (Tables I and II), since the ratio of reactant gases would remain constant throughout the course of the run. Surprisingly, the green solutions gradually turned orange under these conditions, and the color change was associated with enhanced rates of reaction. Product evolution in these cases continued without significant rate retardation until virtually all the reactant gases had been consumed, requiring less than 24 hr. Recharging the final orange solutions with NO and CO in a 4:3 ratio produced results identical with those of run VII. Unfortunately, the color change from green to orange occurred at different times (ranging from 4–6 hr) in seemingly identical runs, and the factors which account for this anomalous behavior remain unclear.

In evaluating the results of Table IV it should be noted that the dilute solutions employed led to very slow reaction rates in which changes in the partial pressures of reactant gases were less than 50 mm. Thus gas concentrations in solution, which should follow Henry's law, remain virtually constant during the course of the kinetic runs. The data of Table IV are internally consistent and may be interpreted as a valid indication of the dependence of the rate of product formation on the reactant gas concentrations.

Reasons for the anomalous reactivity pattern observed in 2:1 NO:CO charges for the 10^{-2} M solutions are unclear at present, but they may relate to mass transfer effects between the solution and gas phases. The change in color from green to orange in these cases with concomitant change in the rate of reaction implicates a different intermediate and reaction mechanism.

Attempts to Isolate Catalytic Intermediates. Numerous attempts were made to isolate the green catalytic intermediate without success, and it appears that this species is stable only under a NO-CO atmosphere. Upon evacuation, the green solutions rapidly become dark reddish orange, and the infrared spectrum of the isolated product shows it to be a mixture of $(AsPh_4)[RhCl_2(CO)_2]$ and the product formed by reaction with NO alone. Addition of triphenylphosphine to the catalytically active solutions results in immediate precipitation of $RhCl(CO)L_2$, $RhCl_2(NO)L_2$,[12] and an unidentified carbonyl containing species (ν_{CO} 1940 cm^{-1}). The complex $RhCl_2(NO)L_2$ is also formed upon addition of triphenylphosphine to the solutions formed by reaction of $[RhCl_2(CO)_2]^-$ with nitric oxide. It should be noted in this context that reaction of $[RhCl_2(CO)_2]^-$ with triphenylphosphine gives $RhCl(CO)L_2$ quantitatively,[6,9] and that $RhCl_2(NO)L_2$ has been obtained by the addition of triphenylphosphine to solutions of $[RhCl(NO)_2]_x$,[13a] $[RhCl_2(NO)]_x$,[13b] and $RhCl_3{\cdot}xH_2O$ under NO.[14]

Neither cooling the green solutions to −78°C nor twofold dilution with hexane induced precipitation. Attempts to obtain an ESR spectrum of the green solution proved unsuccessful. When solutions of $[RhCl_2(CO)_2]^-$ in acidic ethanol were evacuated, cooled to 0°C, and placed under nitric oxide, the resulting green color was maintained for extended periods (12 hr or more). However, it eventually gave way to the reddish color characteristic of the nitrosyl species and no intermediate was obtained. More concentrated solutions of $[RhCl_2(CO)_2]^-$ also resulted in the dark red color and solutions from which only the carbonyl anion and the product(s) formed under NO could be isolated.

In an effort to inhibit product formation and thus increase the probability of isolating an intermediate complex by stabilization, aqueous acid was omitted from the catalyst system, and $[RhCl_2(CO)_2]^-$ in anhydrous ethanol was placed under nitric oxide. A dark yellow solution and an orange-brown precipitate were thus obtained. Initial rapid NO substitution was indicated by the appearance of a carbon monoxide peak in the gas chromatogram and formation of 1 equiv of N_2O within the first 7 hr. If the system was degassed and recharged with nitric oxide at this point, slow production of carbon dioxide continued, implying that one CO remained coordinated to the metal. Further reaction with nitric oxide occurred extremely slowly and was apparently stoichiometric. After 5 days a total of 1 equiv of CO_2 and 2 equiv of N_2O (per mole of rhodium) had been produced. The precipitate which formed during this reaction had an infrared spectrum identical with that of the precipitate formed during run X: 1650 (ν_{NO}), 1500, 1350, 1200, 1100, 930, and 850 cm^{-1}. All of these intense bands were uniformly broad, suggesting a polymeric nitrosyl species containing coordinated nitro or nitrito groups.[15]

Discussion

The results presented above clearly show that $[RhCl_2(CO)_2]^-$ in ethanolic HCl forms a true catalyst for the carbon monoxide reduction of nitric oxide, and that the prolonged induction period previously reported[4] for $RhCl_3{\cdot}xH_2O$ in ethanol is due to initial reduction of Rh(III) to the catalytically active $[RhCl_2(CO)_2]^-$ system. The reductive carbonylation of $RhCl_3{\cdot}xH_2O$,[6] which proceeds slowly in anhydrous ethanol, is accelerated by the addition of a few milliliters of concentrated HCl under a mixed NO-CO atmosphere. Alternatively, the induction period can be shortened by treatment of the $RhCl_3$ solution with CO for several hours prior to exposure to the NO-CO gas mixture.

The need for reduction of Rh(III) to Rh(I) as a prerequisite for the onset of catalytic activity has been reported before, as exemplified by Cramer's[16] study of the rhodium catalyzed dimerization of ethylene. In addition, we have found promotion of reaction 2 without an induction period by a series of Rh(I) complexes including $RhClL_3$, $RhBrL_3$, $RhCl(CO)L_2$, $RhL_3^+BF_4^-$, $[Rh(NBD)Cl]_2$, and $[Rh(COD)Cl]_2$ (L = PPh_3; NBD = norbornadiene; COD = 1,5-cyclooctadiene).[17] Under an NO-CO atmosphere, acidic ethanol solutions of $[RhCl_2(CO)_2]^-$ develop a green color characteristic of catalytic activity within 1 hr, whereas $RhCl_3$ solutions were originally reported[4] to take 8-10 hr to reach a similar appearance.

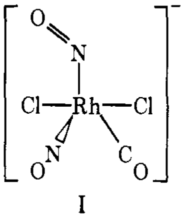
The difference in maximum rates of product formation for equimolar solutions of rhodium trichloride and $[RhCl_2(CO)_2]^-$ in acidic ethanol (see Figure 1) is undoubtedly due to incomplete reduction of rhodium trichloride under the conditions of these experiments. The distinctly orange color of the final solutions in the $RhCl_3$ runs, and the less than 50% recovery of rhodium as $(AsPh_4)[RhCl_2(CO)_2]$ for runs I-III clearly support this view. In addition the observation of infrared bands above 2060 cm^{-1} in crude recovered material establishes the presence of Rh(III) species, such as the halocarbonyl anion $[RhCl_5(CO)]^{2-}$.[6,18] Continued recharging of catalyst solutions produced from $RhCl_3$, however, ultimately results in catalytic activity equivalent to an equimolar amount of the $[RhCl_2(CO)_2]^-$ anion.

In contrast to the $RhCl_3$ system, the truly catalytic nature of $[RhCl_2(CO)_2]^-$ in aqueous acidic ethanol is demonstrated by quantitative recovery of the anion as its $AsPh_4^+$ salt at the end of runs IV-VI, the recharging experiments which reveal no loss of catalytic activity, and the facile, reversible interconversion of the yellow $[RhCl_2(CO)_2]^-$ anion with the green catalytic intermediate. Under a 4:3 ratio of NO:CO, catalysis of reaction 2 proceeds smoothly yielding curve IV which is sigmoidal in shape. The positive curvature in the early stages of the run is associated with a growth in population of the green catalytic intermediate. The negative curvature, indicative of significant retardation of the catalyzed reaction, derives from the fact that consumption of NO and CO in a 2:1 ratio causes a gradual increase in the relative concentration of CO resulting in ultimate regeneration of the starting anion.

When $[RhCl_2(CO)_2]^-$ is reacted under higher ratios of NO:CO or under NO alone, dark red solutions obtain which rapidly turn green under a 4:3 NO:CO ratio, and eventually yield solutions of the starting anion. While the reaction of $[RhCl_2(CO)_2]^-$ with nitric oxide in aqueous acidic ethanol is thus reversible under carbon monoxide, the catalytic cycle clearly does not involve just the coupling of two reactions, as has been suggested by Johnson and Bhaduri[2] for the proposed cycle employing $[Ir(CO)_3L_2]^+$ and $[Ir(NO)_2L_2]^+$ as catalysts for the CO reduction of NO. Rather, catalytic activity in the mixed gas reaction is attributed to the presence of a green nitrosyl carbonyl intermediate which can react directly with NO and CO to produce N_2O and CO_2 without itself undergoing stoichiometric transformation. This catalytically active species is formulated as a nitrosyl carbonyl complex on the basis that it is only observed (at room temperature) under a mixed gas atmosphere, and that the results of spectroscopic studies establish it as an intermediate common to the two limiting reactions (6 and 7). (The stoichiometry of these reactions, though indicated by GC analysis, has not been rigorously established, since the dinitrosyl complex has not been fully characterized.)

$$[RhCl_2(NO)_2]^- + 3CO \rightarrow [RhCl_2(CO)_2]^- + CO_2 + N_2O \quad (7)$$

Since there is virtually no induction period observed upon recharging solutions generated by reaction 6 with NO and CO, whereas 1-2 hr are required to reach maximum rates starting with solutions of the carbonyl anion, it is reasonable to propose this intermediate species as the dinitrosyl carbonyl complex I which must necessarily have at least one bent nitrosyl. Intermediate I is thus isoelectronic with the reactive 20 electron dinitrosyls such as $IrX(NO)_2L_2$ and $Ir(CO)(NO)_2L_2^+$ studied by Haymore and Ibers.[3] The formation of I from the proposed dinitrosyl complex $[RhCl_2(NO)_2]^-$, which is isoelectronic with $Rh(NO)_2L_2^+$,[19] corresponds to simple carbonyl adduct formation, and one can envisage this reaction as a facile equilibrium.



I

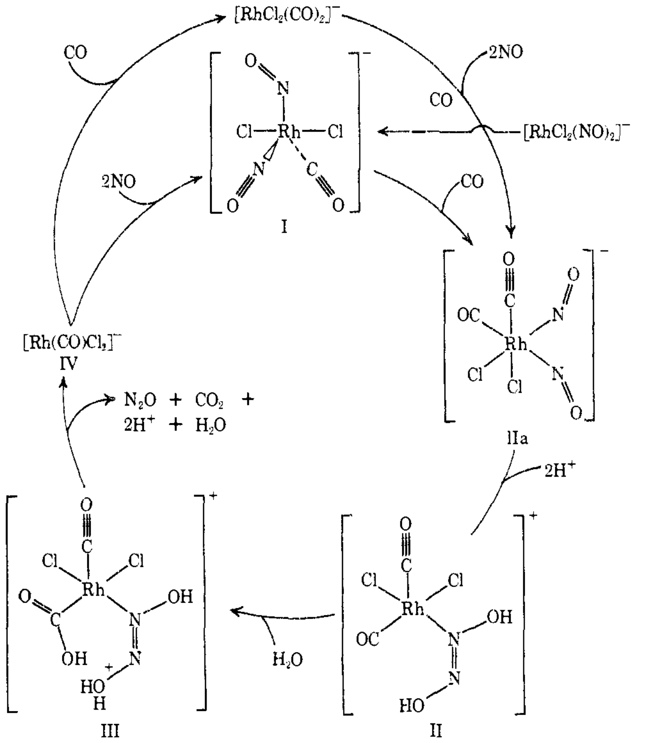
While the reversible formation of I from $[RhCl_2(CO)_2]^-$ has been observed spectrophotometrically, this reaction does not appear to be a simple equilibrium based on GC analysis. When the carbonyl anion is placed under a nitric oxide atmosphere, mainly CO_2 and N_2O are obtained, and little CO is liberated. The latter observation contradicts the notion of simple NO substitution, and instead the formation of I from $[RhCl_2(CO)_2]^-$ is viewed as eq 8.

$$[RhCl_2(CO)_2]^- + 4NO \rightarrow \underset{\text{I}}{[RhCl_2(NO)_2(CO)]^-} + CO_2 + N_2O \quad (8)$$

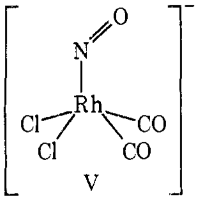
Several mechanistic possibilities can be envisioned for the reaction of I leading to the catalytic conversion of nitric oxide and carbon monoxide into N_2O and CO_2, and they have been put forth previously.[20] The established requirement for water and acid suggest intimate involvement in the catalytic process. In view of the fact that water is required for the formation of CO_2 in the carbon monoxide reduction of rhodium trichloride,[6] and that water is produced in both the acid catalyzed decomposition of hyponitrous acid[27] and in the rhodium trichloride catalyzed disproportionation of NO,[18] it seems likely that water is both consumed in the oxidation of CO and produced in the reduction of NO in the catalytic cycle. The previously proposed pathways thus incorporate water into the product forming steps. Of these possibilities, the one most consistent with all of our observations is outlined in Scheme I.

In accord with the results of kinetic studies, the rate determining step in this scheme is attack by CO on the coordinatively saturated monomeric intermediate I. This is followed, or accompanied, by rapid acid catalyzed ligand migration to form II. The hyponitrite oxygen should be ideally positioned to facilitate attack of hydrogen bonded water molecules on the coordinated carbonyl, both by bringing the reactants into proximity and by enhancing the nucleophilicity of water in acting as a proton acceptor. By analogy with the catalyzed decomposition of hyponitrous acid,[21] formation of N_2O and water from III would be expected to be facile, and reductive decarboxylation is a well-established reactivity pattern.

Scheme I



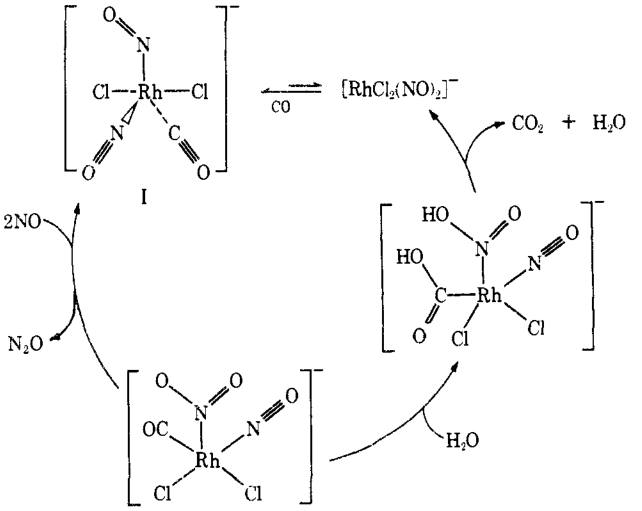
The loss of N_2O and CO_2 from III would be followed by reaction of the coordinatively unsaturated, reactive intermediate IV with either CO or NO to regenerate $[RhCl_2(CO)_2]^-$ or I, respectively. The partitioning of IV between $[RhCl_2(CO)_2]^-$ and I could account for the observed rate retarding effect associated with regeneration of the carbonyl anion. The time dependence of product evolution as shown by curve IV in Figure 1 suggests a change in rate determining step during the course of a 4:3 NO:CO run, and it may be that entry into the catalytic cycle from $[RhCl_2(CO)_2]^-$ replaces the conversion of I to II as the rate determining step after ca. 10-12 hours. This entry most probably involves initial NO adduct formation to give the reactive odd electron complex V which is subsequently attacked by another NO molecule at the metal center to produce intermediate IIa. The conversion of $[RhCl_2(CO)_2]^-$ to I thus requires one completion of the catalytic cycle and involves product formation with the stoichiometry of reaction 8. The observation of an isosbestic point in this system requires that the concentration of intermediates other than I be exceedingly small and necessitates the conclusion that they react as rapidly as they are formed.



V

While the transformation of I to $[RhCl_2(NO)_2]^-$ can easily be envisioned as a simple equilibrium, the formation of a second mole of CO_2 under NO alone, reaction 6, implies the ability of I to undergo further reaction with nitric oxide which is also catalyzed by water and acid. Such a mechanism is illustrated in Scheme II, and provides an alternative pathway for the continuous catalytic reduction of nitric oxide by carbon monoxide. In this sequence reaction of I with nitric oxide yields a nitro nitrosyl derivative and N_2O. The metal promoted disproportionation of NO and

Scheme II

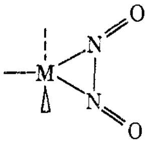


the formation of nitro nitrosyl complexes by reaction with NO have been reported previously for group 8 complexes including $RhClL_3$,[5] $RhCl(CO)L_2$,[5] $IrCl(N_2)L_2$,[3] and $IrBr(NO)_2L_2$ ($L = PPh_3$).[3] Ibers and Haymore[3] have shown that these reactions involve dinitrosyl species of the type $IrX(NO)_2L_2$ as common reactive intermediates, and it is noteworthy that I is isoelectronic with these species. The subsequent oxidation of CO to CO_2 follows in a manner identical with that described in Scheme I, and the conversion of coordinated nitrite to nitrosyl in acidic medium has ample precedent, as for example in eq 9.[22]

$$RuCl(NO_2)(bpy)_2 + 2H^+ \rightarrow RuCl(NO)(bpy)_2{}^{2+} + H_2O \quad (9)$$

The reaction sequence outlined in Scheme II can account for the observation that under higher NO:CO ratios (e.g., 2:1 in run VIII), a different, more reactive catalytic species is serendipitously produced. The color change from green to orange which accompanies accelerated product formation may be associated with an increase in the concentration of $[RhCl_2(NO)_2]^-$ or a related five-coordinate solvate. Further experimentation is obviously required to elucidate the nature of the faster catalytic cycle, and to determine the factors which govern the relative concentrations and reactivities of proposed intermediates in this system.

It is evident that the metal promoted synthesis of N_2O from nitric oxide involves the question of N-N bond formation. Ibers and Haymore, in discussing this problem and the nature of reactive dinitrosyl complexes in the metal promoted disproportionation of NO and the CO reduction of NO originally reported by Johnson and Bhaduri,[2] have proposed[3] viewing these intermediates as dinitrogen dioxide complexes. The intermediates are thus formulated as VI, although their existence as $M(NO^+,NO^-)$ species cannot be ruled out. A possible equilibrium between $M(N_2O_2)$ and



VI

$M(NO^+,NO^-)$ can also be envisioned. Recently, Johnson and co-workers[23] have carried out isotopic labeling experiments on the CO reduction of NO using $Rh(^{15}NO)_2L_2{}^+$ and have interpreted their results as supportive of the dinitrogen dioxide intermediate. However, analysis of their reported observations reveals only that facile exchange of NO with $Rh(NO)_2L_2{}^+$ requires the presence of CO, and that this exchange proceeds rapidly relative to the product forming step. Based on the published data no distinction can be drawn between the two proposed formulations of the reactive dinitrosyls, and it is impossible to say whether dinitrogen dioxide is a ligand in a stable intermediate, a transition state in the conversion of two-coordinated nitrosyls into a hyponitrite type structure, or simply nonexistent.

Moser[24] has recently studied the thermal decomposition of a number of dinitrosyls to yield N_2, N_2O, and NO. Product selectivity (N_2 vs. N_2O) is found to be great in several of these cases, as for instance with $RuCl(NO^+)(NO^-)L_2^+$ [25] which shows a quantitative yield of molecular nitrogen.[24] The importance of the cis dinitrosyl structure is underscored by these results, and Moser's studies start to define the steric and electronic factors which should be useful in future catalyst design.

Finally, the slow catalytic disproportionation of NO by $[RhCl_2(NO)_2]^-$ which we find following reaction 6 appears to be closely related to the observations of Stanko and coworkers.[10] Indeed, GC analysis of the gas mixture reveals that reaction of ethanolic HCl solutions of $[RhCl_2(CO)_2]^-$ with nitric oxide results in consumption of 22 mol of NO per mole of rhodium, with production of 2 mol of CO_2 and 6 mol of N_2O. Thus, if initial stoichiometric conversion according to eq 6 occurs, the mole ratio of NO to N_2O is consistent with slow catalysis of reaction 10. The dinitrosyl complex $[RhCl_2(NO)_2]^-$ differs from the reactive species proposed by Stanko in the oxidation state, but the same mechanism could be operative.

$$4NO + 2CH_3CH_2OH \rightarrow N_2O + 2CH_3CH_2ONO + H_2O \qquad (10)$$

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Catalysis in Oxidation Reactions. II. The Oxalic Acid Catalyzed Oxidation of Iodide[1]

George F. Vandegrift and Jan Roček*

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. *Received July 21, 1975*

Abstract: Oxalic acid acts as a very effective catalyst for the chromic acid oxidation of iodide. At low concentrations, the reaction is first order in oxalic acid, iodide, chromic acid, and hydrogen ions, but becomes zero order in iodide at high iodide concentrations. The proposed mechanism consists of the formation of a termolecular complex $(CO_2)_2CrIO_2^-$ formed from oxalic acid, chromic acid, and an iodide ion followed by its decomposition into an iodine atom and a chromium(V)-oxalic acid complex, $(CO_2)_2CrO_2^-$. It is assumed that the catalytic activity of oxalic acid is due to its ability to stabilize chromium(V). At high iodide concentrations, the formation of the oxalatochromate(VI), $HO_2CCO_2CrO_3^-$, from oxalic acid and $HCrO_4^-$ becomes the rate limiting step of the reaction. The rate of this reaction is about 10^4 higher than previously reported. Indirect kinetic evidence for the formation of the iodochromate ion, $ICrO_3^-$, has also been obtained.

Our observation that oxalic acid[2,3] and hydroxy acids[4-6] have a dramatic accelerating effect on the chromic acid oxidation of alcohols suggested that important new insight into the nature of oxidation processes could be obtained by investigating the effect of oxalic and of substituted carboxylic acid on other oxidation reactions. In this paper we wish to report the results of our study of the effect of oxalic acid on what is certainly the most common of all chromic acid oxidations, the oxidation of iodide ion. Although analytical chemists have been aware for some time[7,8] that the presence