Acknowledgment. This research was supported by the National Science Foundation under Grant NSF DMR8414175. J.K.B. wishes to thank the Laboratoire de Chimie Thèorique, Universitè de Paris Sud, where much of this work was performed, for their hospitality.

Appendix

The calculations for both molecules and solids were of the extended Hückel type[22,23] with the exponents and parameters of Table IV. The modified Wolfsberg-Helmholz formula was used.[24] Except for the icosihexahedron **9**, where the experimental distances found in BeB_3[14] were used, the deltahedra were regular with B-B and Ga-Ga distances of 1.72 and 2.70 Å. The capping atoms used were hydrogen atoms with B-H and Ga-H distances of 1.19 and 1.65 Å. Similar results were found for the electronic structure of these systems independent of whether boron or gallium were used. The same distances were used in the calculations for **6** and **7**. A set of 36 k-points in the irreducible wedge of the hexagonal Brillouin zone were used to calculate the B-B and B-H overlap populations.

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Mechanistic Studies of the Catalytic Reduction of Nitric Oxide by Carbon Monoxide in the Presence of Platinum(II), Copper(I), and Copper(II)

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Received July 31, 1990

A rapid reduction of NO by CO to give N_2O and CO_2 is catalyzed at low temperatures and pressures by an aqueous system comprised of K_2PtCl_4, $CuCl_2$, CuCl, and HCl. Two platinum species, $PtCl_3(CO)^-$ and $PtCl_4^{2-}$, were observed and characterized spectroscopically. The former may also be isolated as $(AsPh_4)[PtCl_3(CO)]$ by quenching the reacting catalyst solution with $AsPh_4^+Cl^-$. During the course of catalysis, CuCl absorbs gaseous CO to yield CuCl(CO), which then reacts with $PtCl_4^{2-}$ to give $PtCl_3(CO)^-$. No carbonylation of $PtCl_4^{2-}$ and hence no catalysis occur in the absence of CuCl. Isotopic labeling studies by using ^{18}O-enriched water as the solvent for the catalysis show that the CO_2 evolved contains nearly the same ^{18}O abundance as in the solvent. In contrast, no ^{18}O from water is incorporated into the product N_2O. These observations clearly establish that both oxygens in CO_2 are from water and exclude a direct oxygen transfer from NO to CO to yield CO_2. Moreover, the high ^{18}O content in CO_2 strongly implies the presence of a rapid process of oxygen scrambling between coordinated CO and water. Indeed, $PtCl_3(CO)^-$ undergoes oxygen exchange with ^{18}O-enriched water extremely rapidly without significant decomposition to give CO_2 in the catalyst solution. The reaction of $PtCl_3(CO)^-$ with CO to give CO_2 is also too slow to account for the CO_2 production. However, by reaction with NO, $PtCl_3(CO)^-$ in the $CuCl-CuCl_2-HCl$ system evolves CO_2 and N_2O rapidly. The presence of $CuCl_2$ or CuCl in the solution is required for the rapid gas production. This reaction is thought to be the process for N_2O and CO_2 production in the catalysis. Consistent with the observed behavior of the system, the results of kinetic studies may be explained in terms of two kinetically distinguishable processes. One is the carbonylation of $PtCl_4^{2-}$ of which the rate shows first-order dependence on each of $[PtCl_4^{2-}]$, P_{CO}, and [CuCl]. The other process is the reaction of $PtCl_3(CO)^-$ with NO and water. Its rate is first order on $[PtCl_3(CO)^-]$, P_{NO}, and $[CuCl_2]$. For the reaction of $PtCl_4^{2-}$ with CO, the enthalpy of activation is 9.1 ± 0.3 kcal mol^{-1} and the entropy of activation is -30.2 ± 0.1 cal K^{-1} mol^{-1}. The corresponding values for the reaction of $PtCl_3(CO)^-$ with NO and H_2O are -1.5 ± 0.3 kcal mol^{-1} and -65.9 ± 0.3 cal K^{-1} mol^{-1}. On the basis of these two processes, a mechanism for the observed catalysis is proposed.

Introduction

The reduction of nitric oxide by carbon monoxide (eq 1) is a subject of considerable interest, particularly in view of its environmental importance and the extensive bond reorganizations involved. The reaction, while highly exothermic, does not occur

$$2NO + CO \rightarrow N_2O + CO_2 \qquad (1)$$

in the absence of a catalyst even at 450 °C.[1] Most studies of the catalysis of reaction 1 used heterogeneous catalysts typically at elevated temperature.[2] The employment of homogeneous systems for this catalytic reaction has been investigated by several groups. Johnson et al. first reported the reaction of $M(NO)_2(PPh_3)_2^+$ (M = Ir, Rh) with CO to give N_2O, CO_2 and $M(CO)_3(PPh_3)_2^+$.[3] Subsequently, the catalysis by these dinitrosyl complexes was explored by Eaymore and Ibers.[4] Efforts by Eisenberg and his co-workers had led to the discovery of an effective catalyst system consisting of $Rh(CO)_2Cl_2^-$, HCl, H_2O, and ethanol for eq 1.[5] By means of an ^{18}O isotopic labeling, they showed that one of the oxygen atoms in the CO_2 product is derived from the water in the reaction medium and not directly from the nitric oxide reactant.[6] In 1978, an aqueous $PdCl_2-CuCl_2-HCl$ system was found to catalyze eq 1 with a rapid rate.[7] A

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Wacker-type mechanism was proposed as the main pathway for the observed catalysis. Recently, we have observed that $[Rh(CO)_2Cl]_2$ in the presence of base catalyzed the reduction of NO by CO to N_2O and subsequently to N_2 at ~100 °C.[8] In view of the high activity of the $PdCl_2$–$CuCl_2$–HCl system in the catalysis of reaction 1, we explored the feasibility of using the closely related $PtCl_4^{2-}$–$CuCl_2$–HCl system to catalyze the same reaction. Surprisingly, it exhibited no catalytic activity toward reaction 1. However, by a slight modification, that is, by addition of CuCl into the solution, the system catalyzes the reaction with a turnover rate greater than that for any other system ever reported. A preliminary communication of this work has appeared.[9]

In this paper, we examine in depth this highly active system including identification of the intermediates, isotopic labeling, and kinetic studies. The results indicate that the roles of CuCl and $CuCl_2$ differ greatly from those known in the reactions catalyzed by the palladium–copper systems.[7] On the basis of these observations, the mechanistic possibilities of the present catalysis are discussed.

Experimental Section

Materials. The following compounds were obtained from the indicated suppliers: K_2PtCl_4 (Strem), $CuCl_2 \cdot 2H_2O$ (Merck), CuCl (Fluka), HCl (Merck), CO, CO_2 (Matheson), NO, N_2O (MG Industries), Ar (Messer Griesheim), $HClO_4$, $LiClO_4 \cdot 3H_2O$ (Merck), and $H_2{}^{18}O$ (20.3% ^{18}O) (MSD). All of these chemicals were used without further purification.

General Procedures. Infrared spectra were recorded on a Perkin-Elmer Model 781 spectrometer and a BOMEM DA 3.002 Fourier-transform spectrometer in 0.10-mm CaF_2 solution cells. Ultraviolet and visible spectra were obtained on a Perkin-Elmer Lambda 5 spectrophotometer. A Varian Aerograph Model 3700 gas chromatograph with a thermal conductivity detector in conjunction with a Shimadzu Model Chromatopac C-R1B microprocessor was used for quantitative analysis of gas mixtures. A Pressure-Lok gas syringe obtained from Precision Sampling Corp. was employed for gas samplings. Separation of CO, NO, N_2, O_2, and Ar was achieved on a 5A molecular sieve column; a Porapak Q column was used to separate CO_2 and N_2O. Helium was employed as the carrier gas for GC analysis. Mass spectral data were obtained on a Jeol JGC-20K/JMS-D100 GC/MS system, the isotopic compositions of CO_2, CO, N_2O, NO, and H_2O were determined by measuring the ratios of the corresponding peak heights. Calibration plots of CO, NO, CO_2, and N_2O were obtained according to the procedures reported previously.[5b] The reaction vessels were a 300-mL ₮ 24/40 (for the kinetic studies) single-neck round-bottom flask and a 32-mL ₮ 14/20 (for the labeling studies) single-neck round-bottom flask connected via a side arm to a three-way stopcock. One stopcock lead was attached to a vacuum pump, and the other was used for addition of gases or stoppered with a septum to allow gas sampling. A ground glass adapter connected the vessel to a mercury manometer. The reaction vessel was immersed in an oil bath to a fixed level. Both the solution and the oil bath were stirred magnetically. A heating element connected via a contact thermometer to a mercury relay was employed to heat the system to a desired temperature. The temperature variation of the oil bath was estimated as ±0.25 °C.

Isolation of $(AsPh_4)[PtCl_3(CO)]$ from the Catalyst Solution. To a reaction vessel (300 mL) was added K_2PtCl_4 (0.125 g, 0.300 mmol), CuCl (0.488 g, 4.53 mmol), $CuCl_2 \cdot 2H_2O$ (1.532 g, 8.98 mmol), LiCl (1.065 g, 25.10 mmol), H_2O (98 mL), and hydrochloric acid (2.00 mL, 12 M). The vessel was connected to a mercury manometer via a ground-glass adapter and was evacuated. The system was flushed with CO once and was then filled with 500 Torr of NO and 250 Torr of CO. The solution was stirred magnetically at ambient temperature for 2 h. To the stirred yellow-green solution was added 0.378 g of $(AsPh_4)Cl \cdot HCl \cdot 2H_2O$ in 15 mL of H_2O. An immediate precipitation was observed. The precipitate was first washed with 10 mL of a 4:1 2-propanol–hydrochloric acid (12 M) mixture and further with 10 mL of 2-propanol three times to yield 0.040 g of the desired product (56%). Anal. Calcd for $AsClH_2OC_{13}OPt$: C, 42.13, H, 2.83; Cl, 14.92. Found: C, 42.31; H, 2.83; Cl, 14.86. IR (KBr): 3059 (w), 2082 (s), 1485 (s), 1442 (s), 1396 (w), 1340 (m), 1315 (m), 1189 (m), 1163 (m), 1090 (s), 1028 (m), 1002 (s), 928 (w), 750 (s), 692 (s) cm^{-1}. The ν_{CO} of the anion appears at 2118 cm^{-1} in H_2O.

^{18}O Labeling Study. A catalyst solution prepared from K_2PtCl_4 (7.2×10^{-4} g, 1.7×10^{-6} mol), $CuCl_2 \cdot 2H_2O$ (1.02×10^{-2} g, 5.99×10^{-5} mol), CuCl (3.00×10^{-3} g, 3.03×10^{-5} mol), LiCl (7.07×10^{-3} g, 1.67×10^{-4} mol), hydrochloric acid (0.10 mL, 0.48 M), and ^{18}O enriched water (0.10 mL, ~20%) was added to a 32-mL reaction vessel that had been filled with 250 Torr of CO and 500 Torr of NO. The solution was magnetically stirred at 27 °C. At 3-, 6-, 10-, and 20-min intervals the gas mixture was sampled by a gas syringe; these samples were injected into a GC/MS instrument for analysis of the isotopic distribution of carbon dioxide, carbon monoxide, nitric oxide, and nitrous oxide. The results are shown in Table I. The abundance of ^{18}O in the aqueous catalyst solution was also analyzed in the mass spectrometer; 11.8% ^{18}O enrichment was found.

Table I. Observed and Calculated ^{18}O Distribution of the CO_2 Product[a] Relative Isotopic Abundance

	distribn		
mass	obsd[a]	calcd (I)[b]	calcd (II)[c]
44	0.796	0.880	0.779
46	0.190	0.119	0.208
48	0.0135	0.000235	0.0138
^{18}O	0.109	0.0597	0.118

[a] The ^{18}O abundance in the aqueous solution was 0.118. The gas phase over the catalyst solution was analyzed four times by GC/MS at 3, 6, 10, and 20 min. The mass ratios obtained, which exhibited no change with time within experimental error, were averaged to give the values listed. [b] Assuming 50% of the oxygen is from water. [c] Assuming both oxygens are derived from water.

Kinetic Runs. A 300-mL reaction vessel was evacuated, charged with CO, NO, and a small amount of Ar (50–100 Torr) and then immersed in the oil bath, which had been heated to the desired temperature. To the vessel was added via a syringe 20.0 mL of a stock solution prepared by diluting a solution containing K_2PtCl_4 (0.0140 g, 3.38×10^{-5} mol), $CuCl_2 \cdot 2H_2O$ (15.35 g, 0.0900 mol), CuCl (4.46 g, 0.0450 mol), and concentrated HCl (50.0 mL, 12.0 M) with water to 1000 mL. The catalyst solution was stirred magnetically at a constant spinning rate. The gas mixture over the solution was sampled and was analyzed by GC periodically. The above stock solution was stored under nitrogen and was used to study the dependence of the catalysis on temperature and CO and NO pressures. Other stock solutions containing various concentrations of catalyst components were used for the preparation of catalyst solutions for studies on Pt^{2+}, Cu^{2+}, Cu^{+}, H^{+}, and Cl^{-} dependence. The detailed conditions of these kinetics runs were described in the Results and Discussion.

Results and Discussion

The reduction of NO by CO in the presence of K_2PtCl_4, $CuCl_2$, CuCl, and HCl proceeds at ambient temperature under an initial total pressure of less than 1 atm. The rate of catalysis varies with temperature, pressure, and the concentration of each catalyst component. Under suitable reaction conditions, a turnover rate of more than 150/h at 30 °C based on N_2O produced can be achieved (see run 2B, Table IV). This catalytic activity is at least 20 times higher than those of the $PdCl_2CuCl_2$–HCl and $Rh(CO)_2Cl_2^-$ systems. The high activity of the Pt system causes a mass-transfer problem with the gas components. If the $[PtCl_4^{2-}]$ used is greater than 10^{-3} M, the solubility rates of NO and CO become the rate-limiting steps for the catalysis of eq 1. To prevent these rates from becoming the rate-limiting process, the concentrations of the platinum species used for kinetic studies were kept below 10^{-4} M.

Identification of Catalytic Intermediates. In order to identify the possible intermediates for the catalysis of reaction 1, the active catalyst solution was examined by UV–vis and IR spectroscopy. An aqueous catalyst solution consisting of 1.00×10^{-2} M of K_2PtCl_4, 4.53×10^{-2} M of CuCl, 8.98×10^{-2} M of $CuCl_2$, 2.51×10^{-1} M of LiCl, and 2.40×10^{-1} M of HCl was stirred in the presence of NO (500 Torr) and CO (250 Torr) gases. A small portion of the solution was withdrawn periodically and was immediately analyzed by a UV–vis spectrophotometer. The spectrum of the solution prior to reaction exhibits two weak absorptions at 390 and 480 nm corresponding to $PtCl_4^{2-}$. After the catalytic reaction proceeded for 5 min, two new peaks at 366 and 420 nm attributed to $PtCl_3(CO)^-$ were observed. The identification of the platinum complexes was made by comparing the UV–vis spectrum of the solution with those of authentic samples. Essentially no further change of the catalyst composition was observed as the catalytic reaction proceeded. The observations

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suggest that the carbonylation of $PtCl_4^{2-}$ to yield $PtCl_3(CO)^-$ takes place rapidly.

Further evidence for the presence of $PtCl_3(CO)^-$ and other components was obtained by quenching the catalysis by injecting excess bulky cation into the solution. Immediate precipitation was observed, and the precipitate was collected and washed thoroughly with a mixture of hydrochloric acid and isopropyl alcohol. When $(AsPh_4)^+(Cl)^-$ was employed as the source for cation, the resulting solid was characterized as $(AsPh_4)[PtCl_3(CO)]$ by elemental analysis and by comparing its IR spectrum with that of an authentic sample prepared independently.[9,10] It is noteworthy that the precipitate before being washed contains a large portion of $(AsPh_4^+)(CuCl_2^-)$, which may be prepared simply by addition of $AsPh_4^+Cl^-$ to a CuCl–HCl aqueous solution. If the filtrate was evacuated to remove all the volatile components, the residue was found to consist of the $PtCl_4^{2-}$ anion in addition to others. The residue exhibits, in addition to the IR absorptions for $AsPh_4^+$, a characteristic peak at 300 cm^{-1} identical with the Pt–Cl absorption of $(AsPh_4^+)_2(PtCl_4^{2-})$ synthesized separately.

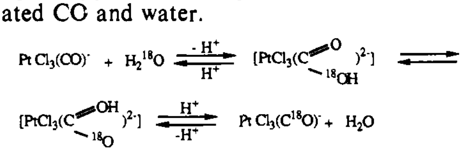
IR analysis of a reacting catalyst solution in the range of the CO stretching frequency provided new insight regarding the catalyst intermediates. In addition to the CO absorption of $PtCl_3(CO)^-$ at 2118 cm^{-1}, another at 2105 cm^{-1} with greater intensity was observed in the spectrum. This peak is attributed to a Cu(I)–CO species, on the basis of the observation that a CuCl–HCl solution stirred under 1 atm of CO also exhibits a carbonyl stretch at the same position.[11] In fact, the absorption of CO by an aqueous CuCl–HCl solution has been known for several decades.[12] It is generally accepted that the copper carbonyl species has a chemical formula of CuCl(CO), although a different structure, $CuCl_2(CO)^-$, has been suggested.[13] The observed rapid carbonylation of $PtCl_4^{2-}$ to give $PtCl_3(CO)^-$ in the catalytic reaction is closely related to the ability of Cu(I) species to absorb free CO. While the carbonylation is complete within 5 min under the catalytic condition, no $PtCl_3(CO)^-$ is detected and consequently no catalysis occurs if CuCl is omitted from the catalyst solution. Thus, the formation of $PtCl_3(CO)^-$ is probably not from a direct reaction of CO with $PtCl_4^{2-}$, but is a process involving the absorption of gaseous CO by $CuCl_2^-$ and the reaction of CuCl(CO) with $PtCl_4^{2-}$ as indicated in eqs 2 and 3. The notion is further

$$CuCl_2^- + CO(g) \overset{K_1}{\rightleftharpoons} CuCl(CO) + Cl^- \qquad (2)$$

$$PtCl_4^{2-} + CuCl(CO) \xrightarrow{k_1} PtCl_3(CO)^- + CuCl_2^- \qquad (3)$$

supported by the observation that addition of a CO-saturated aqueous CuCl–HCl solution via a syringe to a K_2PtCl_4–$CuCl_2$–HCl solution resulted in a rapid conversion of $PtCl_4^{2-}$ to $PtCl_3(CO)^-$. Evidences from kinetic studies for the proposed pathway are presented below. With respect to the intimate mechanism of the carbonylation of $PtCl_4^{2-}$ by CuCl(CO), it is possible that the reaction occurs via steps including formation of a binuclear chloro bridging intermediate, ligand exchange between the two metal centers and breakup of the successor intermediate.

The Source of Oxygen in Carbon Dioxide. Isotopic labeling by using ^{18}O enriched water as the solvent in the catalytic system reveals important features of the catalyst intermediate. Analysis of the gas products by GC/MS shows that essentially no ^{18}O is included in N_2O, but the ^{18}O abundance of CO_2, which is summarized in Table I, is nearly the same as in the solvent, indicating that both oxygens in CO_2 are originally from the aqueous solution. Under the conditions for the ^{18}O-labeling study but in the absence of $PtCl_4^{2-}$, oxygen exchange between CO_2 and labeled water is less than 2.6%. These observations not only exclude the possibility of a direct oxygen transfer from NO to CO but also strongly imply that a rapid oxygen scrambling process (eq 4) occurs between coordinated CO and water.



(4)

A metal hydroxycarbonyl species is generally believed to be the intermediate in oxygen exchange of coordinated CO[14] and in oxidation of CO to CO_2.[6,15] In order to yield a CO_2 product in which both oxygens come from the aqueous solution, the oxygen exchange process of the hydroxycarbonyl intermediate must be much more rapid than the decarboxylation to give CO_2. In fact, we observed by IR spectroscopy that under the catalytic conditions $PtCl_3(CO)^-$ (ν_{CO} = 2118 cm^{-1}), a catalytic intermediate, undergoes oxygen exchange with ^{18}O-enriched water to give $PtCl_3(C^{18}O)^-$ (ν_{CO} = 2072 cm^{-1}), rapidly reaching isotopic equilibrium in less than 5 min with negligible decomposition to yield CO_2.[16]

A comparison of the results of ^{18}O labeling studies for the oxidation of CO to CO_2 mediated by metal complexes to date reveals significant differences in the number of oxygens of CO_2 transferred from water. In the rhodium-catalyzed reduction of NO by CO, only one oxygen in CO_2 comes from water, indicating that no oxygen exchange of the CO ligand with water occurs prior to the formation of CO_2.[6] Several reactions involving oxygen transfer from coordinated NO_2 to CO group also show that one oxygen in the NO_2 is transferred to CO.[17] In the oxidation of CO by Pt^{2+}–Cu^{2+}, we observed statistically 1.5 of the oxygens in CO_2 are from water.[16] Although the same platinum–copper system was used in the oxidation of CO[16] and in the catalysis of reaction 1, the apparent difference in the number of oxygens of CO_2 transferred from water excludes $PtCl_2(CO)_2$ as the intermediate responsible for CO_2 formation in the catalysis of reaction 1. Another possible catalyst intermediate in the present catalysis is $PtCl_3(CO)^-$. While the decomposition of this carbonyl species would yield CO_2 in which both oxygens are from the aqueous solvent, the rate of decomposition is too slow to account for the CO_2 evolution in the observed catalysis. The real structure of the intermediate responsible for CO_2 production is further discussed below.

Chemistry of $PtCl_3(CO)^-$. To gain insight into the role of $PtCl_3(CO)^-$ in the observed catalysis, the chemistry of this anion was investigated under various conditions. For convenience, $(AsPh_4)[PtCl_3(CO)]$ was used for all studies. This salt was synthesized from the carbonylation of $PtCl_4^{2-}$ in a $CuCl_2$–CuCl–HCl solution.[16] Because it cannot be dissolved in aqueous solution, all the reactions were conducted in water–DMF mixtures. The reaction conditions and the amounts of CO_2 and N_2O products are presented in Table II. As indicated in runs I and II, $PtCl_3(CO)^-$ reacts to a significant extent with neither CO nor NO in DMF–HCl–H_2O solution within 30 min. Similarly, only a trace of CO_2 was formed from the reaction of $PtCl_3(CO)^-$ with CO in the presence of $CuCl_2$ or CuCl (runs IV and V). However, when NO was allowed to react with $PtCl_3(CO)^-$ in the presence of CuCl (or CuCl and $CuCl_2$) (runs VII and VIII), rapid evolution of N_2O and CO_2 was observed. The reaction of NO with $PtCl_3(CO)^-$ in the presence of $CuCl_2$ led to a rapid CO_2 formation (run VI) without N_2O evolution. It is notable that although NO is not involved in the stoichiometric reaction, the presence of this gas

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Table II. Results of the Reactions of $PtCl_3(CO)^-$ with NO and (or) CO under Various Conditions[a,b]

	10^4 × amt, mol				*P*, Torr			
run	$CuCl_2$	CuCl	HCl	$ZnCl_2$	$P_i(NO)$	$P_i(CO)$	$P(N_2O)$	$P(CO_2)$
I			4.8			0	1	0
II			4.8			720	0	0
III			4.8		504	368	0	2
IV	5.60		4.8			306	0	2
V		2.81	4.8			295	0	0
VI	5.60		4.8		779		0	46
VII		2.77	4.8		871		15	14
VIII	5.60	2.80			912		74	79
IX				3.23	791		54	54
X					891		19	19

[a] Each reaction solution in runs I–XI contains 1.87×10^{-5} mol of $(AsPh_4)[PtCl_3(CO)]$, 0.40 mL of DMF, and 0.10 mL of H_2O in a 4.5-mL flask in addition to the components specified in the table. The solution was stirred magnetically at 27 °C for 30 min prior to GC sampling. [b] The partial pressure of CO_2 in the 4.5-mL reaction flask should be 83 Torr at 27 °C, if all CO in $(AsPh_4)[PtCl_3(CO)]$ used is converted to CO_2 and all CO_2 is in the gas phase. Solubility tests indicate that less than 7% of CO_2 is in the DMF solution.

is necessary for a fast CO_2 evolution. Presumably, Cu(II) is reduced to Cu(I) species as CO is oxidized to CO_2 in the reaction (eq 5). A comparison of the results in runs I–X clearly show

$$2Cu(II) + PtCl_3(CO)^- + H_2O + Cl^- \rightarrow 2Cu^+ + CO_2 + 2H^+ + PtCl_4^{2-} \quad (5)$$

that the presence of HCl inhibits the production of N_2O and CO_2. Finally, in a DMF–H_2O solution, the rates of formation of both N_2O and CO_2 from the reaction of $PtCl_3(CO)^-$ with NO and water are enhanced in the presence of $ZnCl_2$.

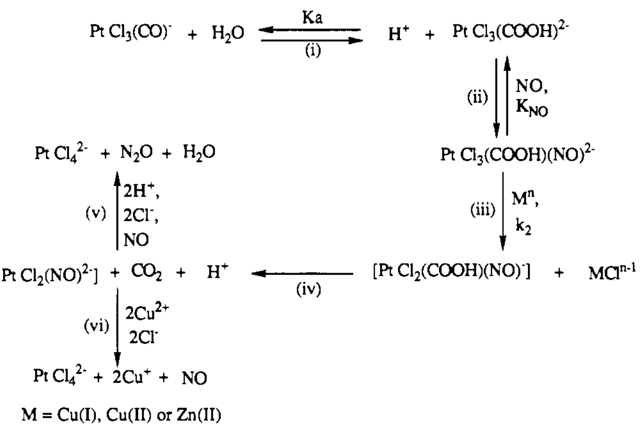
For comparison, the reaction of $PtCl_3(CO)^-$ with NO in aqueous solutions was also investigated. $PtCl_3(CO)^-$ was generated in situ from the reaction of CO with $PtCl_4^{2-}$ in an aqueous CuCl–$CuCl_2$–HCl–LiCl solution followed by vacuum removal of the gases. The solution then was stirred under 1 atm of NO for 30 min, producing 0.93 equiv of CO_2 and 0.72 equiv of N_2O per $PtCl_3(CO)^-$. In addition, a UV–vis spectral study indicates that $PtCl_3(CO)^-$ is converted to $PtCl_4^{2-}$ after the reaction. This experiment was repeated except that the solution was stirred under air for 1 h to oxidize all CuCl existing in the solution, prior to being stirred under 1 atm of NO. To ensure that no more CuCl was present, the solution was further stirred under 1 atm of CO for 10 min. No CuCl(CO) absorption was observed in the IR spectrum of the solution. By this means, the reaction of $PtCl_3(CO)^-$ with NO was carried out in the absence of CuCl in an aqueous $CuCl_2$–HCl–LiCl solution. The reaction yielded 0.85 equiv of CO_2 and 0.71 equiv of N_2O per $PtCl_3(CO)^-$ in 30 min, in contrast to the observation that only CO_2 was produced from the same reaction in a DMF–water mixture (run VI).

Presumably, the difference in results arise from a change in the oxidizing ability of the copper(II) species in an aqueous solution and in a DMF–water mixture. It is known that the coordination of Cl^- ion to Cu(II) is sensitive to the nature of the solvent.[18-21] Consequently, the change in oxidizing ability of Cu(II) is likely due to a change in the number of Cl^- ions coordinated to a Cu(II) ion in these two solvents.

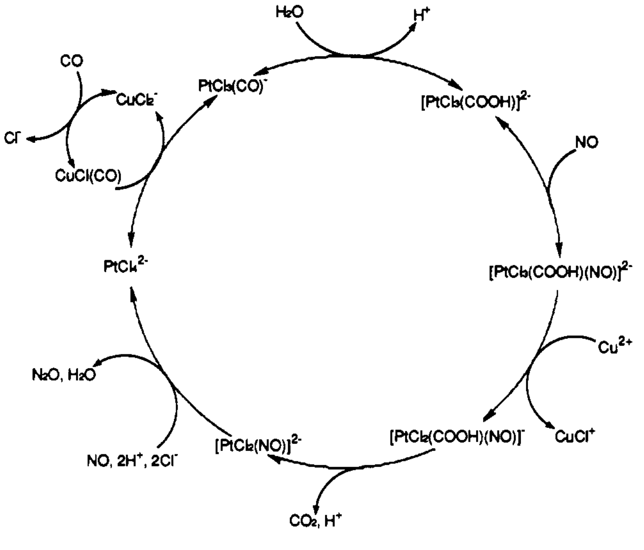
The rapid production of CO_2 and N_2O from the reaction of $PtCl_3(CO)^-$ and NO in the presence of CuCl and (or) $CuCl_2$ strongly suggests that this reaction is the key pathway for gas evolution in the observed catalysis. On the basis of the results of preceding experiments, the stoichiometry may be expressed according to

$$PtCl_3(CO)^- + 2NO + Cl^- \rightarrow PtCl_4^{2-} + N_2O + CO_2 \quad (6)$$

Scheme I



Scheme II



Although direct evidence for the presence of the reaction intermediates for eq 6 is lacking, the observed data in Table II and the results of isotopic labeling studies can be accommodated by the mechanism depicted in Scheme I. On the basis of this scheme, the chemistry of $PtCl_4^{2-}$ and kinetic results presented in the following sections, we propose the catalytic cycle as shown in Scheme II for reaction 1 using the K_2PtCl_4–$CuCl_2$–CuCl–HCl system.

The observed isotopic equilibrium between $PtCl_3(CO)^-$ and water and the negative effect of H^+ concentration on the rate of reaction 6 support the establishment of preequilibrium between a Pt–CO and a Pt–COOH species. Although no platinum–NO complex is detected spectroscopically, the requirement of the presence of NO for rapid CO_2 evolution strongly suggests that a NO group is coordinated to the platinum species during the CO_2 formation process. The enhancement of gas evolution by the presence of CuCl or $CuCl_2$ is interpreted as a Lewis-acid-assisted

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Table III. Dependence of the Initial Rate on the Concentration of K_2PtCl_4 at 30 °C[a]

run	$10^5[K_2PtCl_4]$, M	P_{NO}, Torr	P_{CO}, Torr	$-\Delta P_{NO}/2\Delta t$[b], Torr s^{-1} × 10^{-3}
1A	2.11	447	217	0.92 ± 0.03
1B	2.54	447	217	1.12 ± 0.02
1C	3.38	445	218	1.65 ± 0.02
1D	5.07	446	223	2.27 ± 0.03
1E	6.76	445	226	3.10 ± 0.03

[a] The catalyst solution (20.0 mL) in each run contains $CuCl_2$ (9.00 10^{-2} M), CuCl (4.51 × 10^{-2} M), HCl (0.605 M), and K_2PtCl_4 at the concentration listed in the table. [b] The estimated errors are listed as standard deviations from linear regression. Systematic errors of ~3% are not included.

removal of a chloride ion from a platinum hydroxycarbonyl intermediate, providing a vacant site for the subsequent decomposition to give CO_2. This hypothesis is further supported by the observation that $ZnCl_2$, which is unlikely to participate in any redox reaction under the reaction conditions, also enhances the gas production (run IX).

One interesting question about the mechanism in Scheme I is why the coordination of NO to $PtCl_3(COOH)^{2-}$ makes the CO_2 evolution rapid. As we have pointed out previously, in order to facilitate CO_2 formation, it is necessary to replace one chloride ligand in $PtCl_3(COOH)^{2-}$ by a π-acid ligand whose presence greatly stabilizes the reduced Pt species through back-donation during the process of decarboxylation.[16] Replacement of Cl^- in $PtCl_3(COOH)^{2-}$ by NO or CO appears to meet such a requirement. However, from a comparison of the rates of the catalytic reaction 1 and of the oxidation of CO in the aqueous $PtCl_4^{2-}$–CuCl–CuCl–HCl–LiCl system,[16] it is estimated that the substitution reaction by NO is at least 20 times as rapid as by CO.[9] The unpaired electron and the dual bonding mode of NO are likely responsible for the rapid substitution reaction. It is expected that the addition of NO to $PtCl_3(COOH)^{2-}$ gives a 17-electron $PtCl_3(COOH)NO^{2-}$ in which the NO ligand is bent and the metal center is formally Pt(III). As a chloride is removed from the platinum intermediate (step iii), a bent-to-linear interchange of the coordinated NO would occur to compensate the loss of electron in the Pt center. Thus, the resulting $PtCl_2(COOH)NO^-$ is also 17-electron with the NO linear and the metal in the I oxidation state. Facile ligand substitutions of nitrosyl complexes ascribed to the dual bonding modes have been observed previously.[22]

Kinetic Investigations. Kinetic investigations were performed by the method of initial rates. The gas mixture over the catalytic solution was periodically sampled and analyzed by gas chromatography. Peak areas were converted to partial pressures by using calibration plots and corrected to their values at 27 °C by employing an internal argon standard. The disappearance of both NO and CO was observed to be linear with time for the first few hours. The former showed an initial rate twice as great as the latter within experimental error. As the NO peak is sharper and the area exhibits better reproducibility, its rate of disappearance was employed for all calculations.

Effect of Platinum Concentration. The dependence of the initial rate on platinum concentration was studied at constant partial pressures of NO and CO (Table III) and by using solutions with initial platinum concentrations in the range 2.11 × 10^{-5} to 6.76 × 10^{-5} M. Plots of the partial pressures of NO vs time were linear for these kinetic runs. The slopes of these lines determined by a least-squares fit of the data are presented in Table III. A plot of ln ($-\Delta P_{NO}/2\Delta t$) vs ln $[K_2PtCl_4]$ is linear with a slope of 1.04 ± 0.05, establishing a first-order dependence on the platinum concentration.

Effect of NO and CO Partial Pressures. To avoid variations in concentration, these kinetic runs were carried out by using a stock solution consisting of K_2PtCl_4 (3.38 × 10^{-5} M), $CuCl_2$ (9.00 × 10^{-2} M), CuCl (4.51 × 10^{-2} M), and HCl (0.600 M). Again, the partial pressure of NO was found to decrease linearly with time for the first few hours. The slopes of these lines and the detailed reaction conditions are listed in Table IV. Although these kinetic data show that the rate of NO disappearance increases as the partial pressure of NO or CO increases, it is not a simple first- or second-order dependence on the partial pressure of gas reactants.

Table IV. Effect of Partial Pressures of NO and CO on the Catalytic Rate[a]

run	P_{NO},[b] Torr	P_{CO},[b] Torr	P_{NO}/P_{CO}	$-\Delta P_{NO}/2\Delta t$,[c] Torr s^{-1} × 10^{-3}	$1/k_0$, M s
2A	212	463	0.458	1.63 ± 0.02	4.38 ± 0.06
2B	331	341	0.971	2.02 ± 0.02	5.58 ± 0.06
2C	394	276	1.43	1.92 ± 0.03	6.90 ± 0.12
2D	444	228	1.95	1.80 ± 0.03	8.34 ± 0.18
2E	475	206	2.30	1.73 ± 0.03	9.24 ± 0.18
2F	364	187	1.95	1.43 ± 0.02	8.52 ± 0.12
2G	297	157	1.89	1.20 ± 0.03	8.34 ± 0.24
2H	225	121	1.86	0.97 ± 0.05	7.86 ± 0.36

[a] [CO] = $[K_2PtCl_4]$ = 3.38 × 10^{-5} M, T = 30.0 °C. The concentrations of other components in the catalyst solutions are the same as those listed in Table III. [b] The average pressure during the period of catalysis. [c] The estimated errors are listed as standard deviations from linear regressions.

To find a suitable rate equation properly describing the dependence of rate on the partial pressures of NO and CO, it is necessary to assume that there are two major platinum species present in the catalytic reaction. One species readily reacts with CO, while the other with reacts NO. On the basis of the previous studies, it is undoubtedly that one platinum intermediate should be $PtCl_4^{2-}$, which reacts with CO to give the other $PtCl_3(CO)^-$. The latter species then reacts with NO to yield CO_2 and N_2O. During the course of catalysis, a steady-state condition is established such that the platinum is distributed between $PtCl_3(CO)^-$, $PtCl_4^{2-}$, and other intermediates of negligible concentration. Despite that the rate constants may differ greatly, the rates of each individual step in the catalytic cycle are the same. Under the assumption that the carbonylation of $PtCl_4^{2-}$ and the reaction of $PtCl_3(CO)^-$ with NO are both of first order on the partial pressures of CO and NO respectively, the rate for the observed catalysis may be represented according to

$$-dP_{NO}/2dt = \text{rate} = k_{01}P_{CO}[PtCl_4^{2-}] = k_{02}P_{NO}[PtCl_3(CO)^-] = k_0C_0P_{NO} \qquad (7)$$

Thus, if we assume that C_0 is the total platinum concentration ($C_0 = [PtCl_4^{2-}] + [PtCl_3(CO)^-]$) and k_0 is equal to the observed catalytic rate constant (eq 7), the expressions depicted in eqs 8–10 can be obtained. At constant P_{NO} and P_{CO} as in runs 1A–1E, eqs 7 and 9 predict that the catalytic rate has first-order dependence on the total platinum concentration, even though two major platinum species are present. This is in agreement with the results shown in Table III.

$$[PtCl_3(CO)^-] = \frac{k_{01}C_0P_{CO}}{k_{02}P_{NO} + k_{01}P_{CO}} \qquad (8)$$

$$\text{rate} = (k_0C_0P_{NO}) = \frac{k_{02}P_{NO}(k_{01}C_0P_{CO})}{k_{02}P_{NO} + k_{01}P_{CO}} \qquad (9)$$

$$\frac{1}{k_0} = \frac{1}{k_{02}} + \frac{1}{k_{01}}\frac{P_{NO}}{P_{CO}} \qquad (10)$$

The calculated values of $1/k_0$ at 30 °C are also given in Table IV. As depicted in Figure 1, a plot of $1/k_0$ vs P_{NO}/P_{CO} does yield a straight line. It should be noted that the relationship in the figure is also valid even at very different total pressures of P_{NO} and P_{CO} (runs 2F–2H). The results strongly support the assumption that two major platinum species exist during the catalytic reaction. The slope and intercept of the straight line give k_{01} of 0.373 ±

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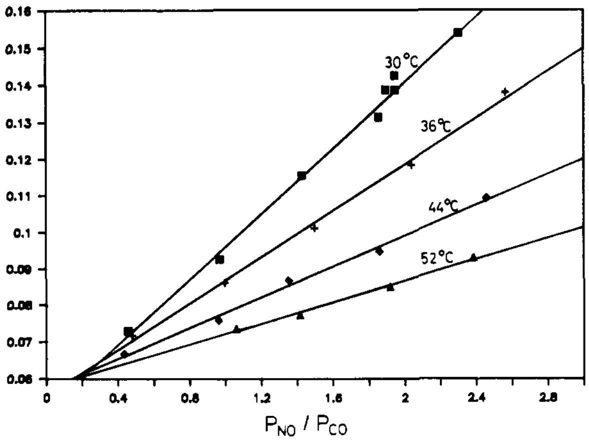

Figure 1. Plots of $1/k_0$ vs P_{NO}/P_{CO} at various temperatures. Each catalyst solution contains $CuCl_2$ (9.00×10^{-2} M), CuCl (4.51×10^{-2} M), HCl (0.605 M), and K_2PtCl_4 (3.38×10^{-5} M).

Table V. Rate Constants at Various Temperatures

temp, °C	k_{01},[a] s^{-1} M^{-1}	k_{02},[a] s^{-1} M^{-1}
30	0.373 ± 0.008	0.325 ± 0.008
36	0.528 ± 0.017	0.302 ● 0.010
44	0.793 ± 0.034	0.293 ± 0.007
52	1.123 ± 0.070	0.292 ± 0.005

[a] The estimated errors are listed as standard deviations from linear regressions.

Table VI. Activation Parameters for the Observed Catalysis

	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] cal K^{-1} mol^{-1}	$\Delta G_{298}{}^{\ddagger}$,[a] kcal mol^{-1}
k_{01}	9.1 ± 0.3	-30.2 ± 0.1	18.2 ± 0.3
k_{02}	-1.5 ± 0.3	-65.9 ± 0.3	18.1 ± 0.4

[a] The estimated errors are listed as standard deviations from linear regressions.

0.008 s^{-1} M^{-1}, and k_{02} of 0.325 ± 0.008 s^{-1} M^{-1}. It is noteworthy that these values are not true rate constants for elementary steps, as they involve terms from a number of equilibria that are discussed later.

Effect of Temperature. The temperature dependence of the observed catalysis was investigated by using the catalyst from the same stock solutions. Plots of $1/k_0$ at various temperatures as functions of P_{NO}/P_{CO} are also linear (Figure 1). The values of k_{01} and k_{02} at 30, 36, 44, and 52 °C from the slopes and intercepts of these lines are presented in Table V. As shown in Figure 2, plots of ln (k/T) (where $k = k_{01}$ or k_{02}) vs $1/T$ also yield straight lines. The apparent entropy and enthalpy of activation for k_{01} and k_{02}, calculated according to the Eyring equation from the intercepts and slopes of these lines, are listed in Table VI.

Effect of CuCl Concentration. The influence of CuCl on the rate of catalysis was also studied by using a stock solution consisting of the catalyst components with the same concentrations except CuCl as in the study of the effect of NO and CO. The desired CuCl concentration was obtained by adding a weighed amount of CuCl to 20.0 mL of the catalyst solution. In Figure 3, a plot of $1/k_0$ as a function of $(1/[CuCl])(P_{NO}/P_{CO})$ is linear with a slope of 0.096 ± 0.001 M^2 s and an intercept of 3.9 ± 0.4 M s. A comparison of eq 10 with this plot shows that the slope is equal to $[CuCl]/k_{01}$, while the intercept is identical with $1/k_{02}$. The results clearly establish a first-order dependence of k_{01} on the CuCl concentration in accordance with the observation that the carbonylation of $PtCl_4^{2-}$ requires the presence of CuCl. At [CuCl] = 0.0451 M, the values of k_{01} and k_{02} calculated from the plot are 0.470 s^{-1} M^{-1} and 0.257 s^{-1} M^{-1}, respectively, in reasonable agreement with the value of 0.373 s^{-1} M^{-1} and 0.325 s^{-1} M^{-1} from the plot in Figure 1.

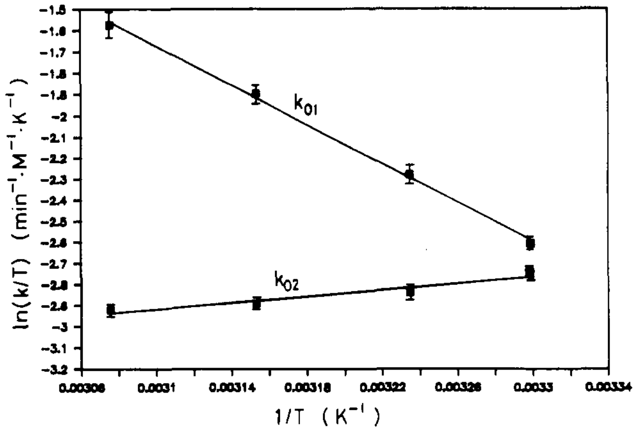

Figure 2. Eyring plots for k_{01} and k_{02} over the temperature range 30–52 °C.

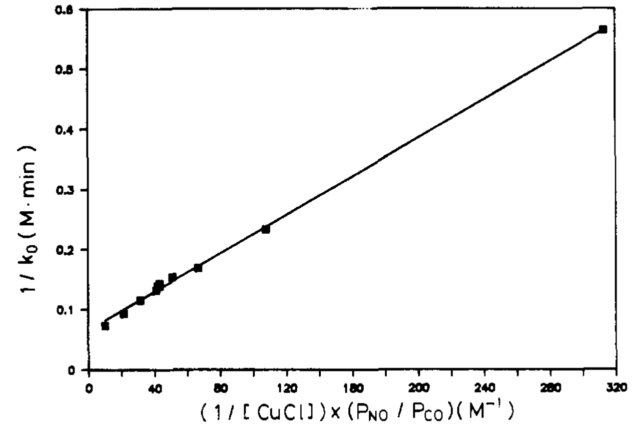

Figure 3. Effect of CuCl on the observed catalysis. [CuCl] is referred to the total concentration of CuCl added. Except for the concentration of CuCl, the catalyst composition of each run is the same as that in run 1C (Table III). The reaction temperature is 30 ± 0.25 °C.

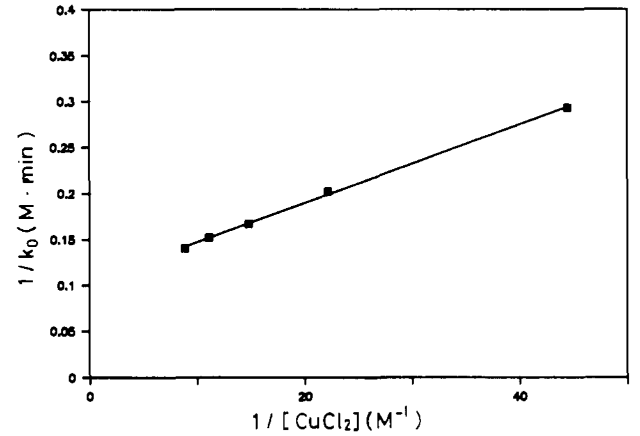

Figure 4. Effect of $CuCl_2$ on the observed catalysis. $[CuCl_2]$ is referred to the total concentration of $CuCl_2$ added. Except for the concentration of $CuCl_2$, the catalyst composition of each run is the same as that in run 1C (Table III). The reaction temperature is 30 ● 0.25 °C.

Effect of $CuCl_2$ Concentration. The influence of changing $CuCl_2$ concentration on the rate of the observed catalysis was examined according to a procedure similar to that for studying the effect of CuCl concentration. As shown in Figure 4, a plot of $1/k_0$ as a function of $1/[CuCl_2]$ is also linear with a slope of 0.256 ± 0.005 M^2 s and an intercept of 6.24 ± 0.12 M s. In these kinetic runs, the ratio P_{NO}:P_{CO} varies between 1.98 and 1.90 and can be seen as a constant value within experimental error. The observed linear plot correlates well with the notion that $CuCl_2$ acts as a Lewis acid in the reaction of $PtCl_3(CO)^-$ with NO and water (vide supra) and implies that k_{02} in eq 10 is first order in $CuCl_2$ concentration. Thus, the slope of the plot is equal to $[CuCl_2]/k_{02}$, while the intercept is identical with $(1/k_{01})(P_{NO}/P_{CO})$. A comparison of eq 10 with the plot also enables us to calculate the values of k_{01} and k_{02} at various concentration of $CuCl_2$. At $[CuCl_2] = 0.0900$ M and $P_{NO}/P_{CO} = 1.98$ the values of k_{01} and k_{02} are 0.317 and 0.352 s^{-1} M^{-1}, respectively. These are close to those obtained from the plot in Figure 1.

Effect of H^+ and Cl^-. The observed catalysis also exhibits great dependence on the concentration of hydrogen ion and chloride ion. Qualitative results indicate that a 2-fold increase of $[H^+]$ leads to a decrease of the rate to ca. half that of the original value. A similar dependence was also obtained for chloride ion.

Although the mechanism proposed for the carbonylation of $PtCl_4^{2-}$ in eqs 2 and 3 does not consist of a direct reaction of $PtCl_4^{2-}$ with CO or with $CuCl_2^-$, the rate law derived from these equations does show a first-order dependence on both $P_{CO}[PtCl_4^-]$ and $[CuCl_2^-]$ (eq 11) wholly in agreement with observed kinetic results.

$$\text{rate} = k_1K_1[CuCl_2^-][PtCl_4^{2-}]P_{CO}/[Cl^-] \qquad (11)$$

A comparison of eqs 7 and 11 leads to the relation

$$k_{01} = k_1K_1[CuCl_2^-]/[Cl^-] \qquad (12)$$

In aqueous solution, the side reaction (step vii) in Scheme I is negligible compared to the N_2O formation reaction. Assuming that the first two steps are completely reversible reactions and step iii is rate limiting, the rate law of NO disappearance derived from Scheme I is

$$-dP_{NO}/2dt = K_aK_{NO}k_2P_{NO}[H_2O][Cu^{2+}][PtCl_3(CO)^-]/[H^+] \qquad (13)$$

A comparison of eqs 7 and 13 leads to the following expression:

$$k_{02} = K_aK_{NO}k_2[H_2O][Cu^{2+}]/[H^+] \qquad (14)$$

The relationship is consistent with the experimental results that k_{02} is first-order in $[CuCl_2]$ and depends inversely on $[H^+]$.

The observed slightly negative $\Delta H^\ddagger$ for k_{02} should be considered with caution. In view of the small absolute value of $\Delta H^\ddagger$ and the relative large deviation accompanied, it appears to be more appropriate to think that this parameter is small and close to a zero value. It is known in literature that a reaction pathway requiring one or more equilibria prior to the rate-limiting step can easily have a small or even negative $\Delta H^\ddagger$.[23,24] The large negative value of $\Delta S^\ddagger$ (-65.9 cal K^{-1} mol^{-1}) for k_{02} is expected from the proposed mechanism. In Scheme I, the formation of $PtCl_3(COOH)^{2-}$ is a charge-separation reaction; the dissolution of gaseous NO and the NO coordination are all greatly entropy-decreasing steps. Although the enthalpy and entropy of activation for the carbonylation of $PtCl_4^{2-}$ and the reaction of $PtCl_3(CO)^-$ with NO and water are different, the Gibbs free energies of activation of both reactions (Table VI) are nearly the same.

In spite of the active involvement of NO in the CO_2 formation process, the present studies provide little mechanistic information for N_2O evolution. However, they do indicate that N_2O production is relatively fast and is not involved in the rate-determining steps. At the present stage, it would be appropriate to assume that synthesis of N_2O involves formation of a dinitrosyl–Pt(0) (assuming NO is neutral) complex, coupling of the dinitrosyl groups, and protonation of the resulted hyponitrite species to give N_2O, H_2O, and a Pt(II) complex. In the catalytic cycle, CuCl is a CO carrier while $CuCl_2$ is acting as a cocatalyst assisting the removal of a Cl^- ligand from a platinum intermediate. This role as a Lewis acid is previously unreported for the palladium–copper-catalyzed reactions in which the Cu(I) and Cu(II) species generally act as a redox couple.[24–29] It is interesting to compare the behavior of the present platinum system and the palladium system reported previously[7] in the catalysis of reaction 1. Under the same catalytic conditions, the palladium system converts all of the CO to CO_2 in 2 h. This was followed by a much slower consumption of NO and production of N_2O over a period of 24 h. On the other hand, the platinum system consumed CO and NO in a ratio of approximately 1:2 with no change of this ratio throughout the period of catalysis. The observations indicate that the mechanisms for the catalysis of eq 1 by the palladium and the platinum systems are different. While the mechanism for the platinum system has been depicted in Scheme II, it appears that the palladium system follows a Wacker-type mechanism.

Concluding Remarks

We have demonstrated that the catalysis of reaction 1 by the present platinum system may be kinetically divided into two processes. One is the reaction of CO with $PtCl_4^{2-}$ to $PtCl_3(CO)^-$, the other is the reaction of $PtCl_3(CO)^-$ with water and NO yielding N_2O and CO_2. As a consequence of the fast oxygen scrambling, ^{18}O isotopic labeling studies have shown that statistically both oxygens in the CO_2 product are from water. The roles of Cu^+ and Cu^{2+} species in the present catalysis differ greatly from those known for the palladium–copper-catalyzed reactions and have not been previously recognized. Thus, it should be interesting to see whether such roles are also applied to some palladium–copper systems. Studies on these aspects are in progress.

Acknowledgment. We thank the National Science Council of the Republic of China for the financial support of this work.

Registry No. NO, 10102-43-9; CO, 630-08-0; K_2PtCl_4, 10025-99-7; $CuCl_2$, 7447-39-4; CuCl, 7758-89-6; HCl, 7647-01-0.

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