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REDUCTION OF NITRIC OXIDE BY CARBON MONOXIDE AND WATER IN AN AQUEOUS ALKALINE SOLUTIONS OF HEXARHODIUM HEXADECACARBONYL AND TETRARHODIUM DODECACARBONYL COMPLEXES

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The reduction of nitric oxide to ammonia was examined in an aqueous KOH solution of $Rh_6(CO)_{16}$ or $Rh_4(CO)_{12}$ complex. It is confirmed that the water gas shift reaction is incorporated with this reaction, providing hydrogen for ammonia formation.

Homogeneous catalytic reduction of nitric oxide by carbon monoxide[1,2) or ammonia[3,4) to form N_2O and N_2 has recently been demonstrated by some mononuclear transition metal complexes. However, there has been no report about the formation of NH_3 from NO-H_2 reaction in the homogeneous system. On the other hand, homogeneous catalysis of the water gas shift reaction (WGSR) by some mononuclear carbonyl complexes[5,6) and also by some carbonyl cluster complexes[7) has been utilized as a hydrogen source for the hydroformylation reaction of olefins[8) and the reduction of aromatic nitro compounds[9).

In this communication, we report for the first time, that the catalytic reduction of nitric oxide, coupled with the water gas shift reaction, occurs to form not only N_2O and N_2 but also NH_3, by an aqueous KOH solution of $Rh_6(CO)_{16}$ or $Rh_4(CO)_{12}$ complex at 20°C and under atmospheric pressure. The reaction was performed in a closed gas circulation system (total volume, ca 320 cm^3) containing a vigorously stirred solution of the complex. The composition of the gas phase was analyzed by gas chromatography, with molecular sieve column for H_2, N_2, NO and CO; Chromosorb 103 column for CO_2 and N_2O at room temperature (with Ar carrier, the detection limit for H_2 was 0.2 μmol and for others, 1 μmol by TCD). The amount of ammonia in the solution was analyzed colorimetrically using Nessler's reagent after vacuum distillation of the complex solution.

When a mixture of NO (0.1∼0.7 mmol) and CO (1∼5 mmol) was introduced into the aqueous solution (100 ml) of KOH (0.1∼9 M) and $Rh_6(CO)_{16}$ ($1x10^{-5}$∼ $7x10^{-5}$ mol), N_2O, N_2 and NH_3 were produced in a few hours as shown in fig. 1. Produced CO_2 was not detected in the gas phase because of the strong alkaline solution, but when the solution was neutralized by HCl after the reaction, reasonable amount of CO_2 was detectable by gas chromatography. After gaseous NO was consumed, H_2 was produced by WGSR, indicating the inhibition or coupling of WGSR with the reduction of NO. The same reaction proceeded in an aqueous KOH solution of $Rh_4(CO)_{12}$ complex. The rate and the selectivity for the product formation were quite similar to the case of $Rh_6(CO)_{16}$ complex, which suggests the existence of the similar catalytically active species in both cases. To investigate the role of formed hydrogen as the reducing agent of NO, hydrogen gas (1 mmol) was added during NO-CO reaction. No effect was observed for the product formation rates, which indicates that this system does not catalyze NO-H_2 reaction to form ammonia. The reaction did not proceed at all only with KOH or rhodium cluster complexes in the solution. As the reaction proceeded the deactivation of the complex took place gradually. But the turnovers of this reaction estimated from the consumed amount

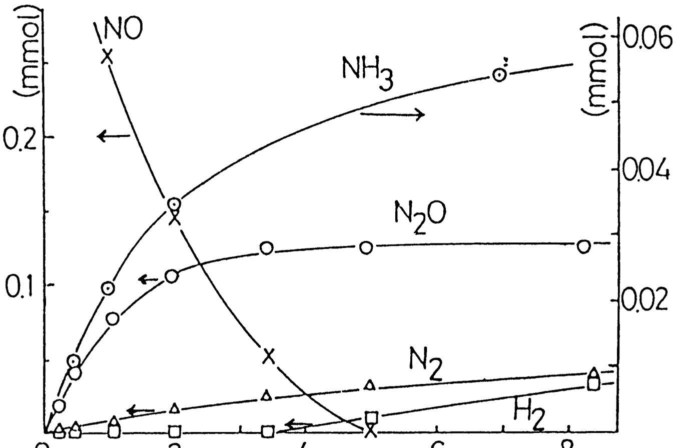

Fig.1. NO-CO-H_2O reaction by aqueous KOH solution of $Rh_6(CO)_{16}$ complex at 20°C. CO=3.7mmol(not plotted), NO=0.68mmol, $Rh_6(C))_{16}$=$2.4x10^{-5}$mol in 100ml(KOH=0.89 M)

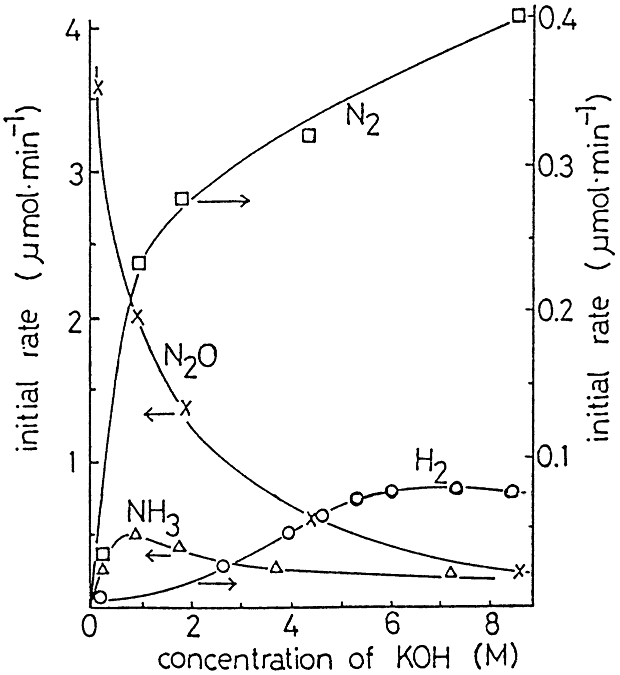

Fig.2. Dependence of the initial rates of N_2O, N_2, NH_3 and H_2(by WGSR) formation upon the conc. of KOH at 20°C. CO=3.1mmol, NO=0.41mmol, $Rh_6(CO)_{16}$=$2.0x10^{-5}$mol in 100 ml KOH-aqueous solution.

of NO against Rh cluster complex employed, was more than 100 before significant loss of the catalytic activity. When the concentration of KOH or the partial pressure of nitric oxide was very high, some black material precipitated during the reaction, causing the loss of the catalytic activity.

The dependence of the initial rates of N_2O, N_2 and NH_3 formation upon the concentration of KOH were examined in the case of $Rh_6(CO)_{16}$ complex, as summerized in fig. 2. When the concentration of KOH was low, the main product was N_2O, but as the concentration increased, the rate of N_2O formation decreased drastically. On the other hand, the rate of N_2 formation increased considerablly with the increase of KOH concentration and became comparable to that of N_2O formation at higher concentrations. The initial rate of ammonia formation exhibited the different dependence, which was rather similar to the case of WGSR in the same system. To examine the correlation between these two reactions, the following experiment was carried out as shown in fig. 3. First of all, only carbon monoxide was introduced into the aqueous KOH solution of $Rh_6(CO)_{16}$ or $Rh_4(CO)_{12}$ complex and

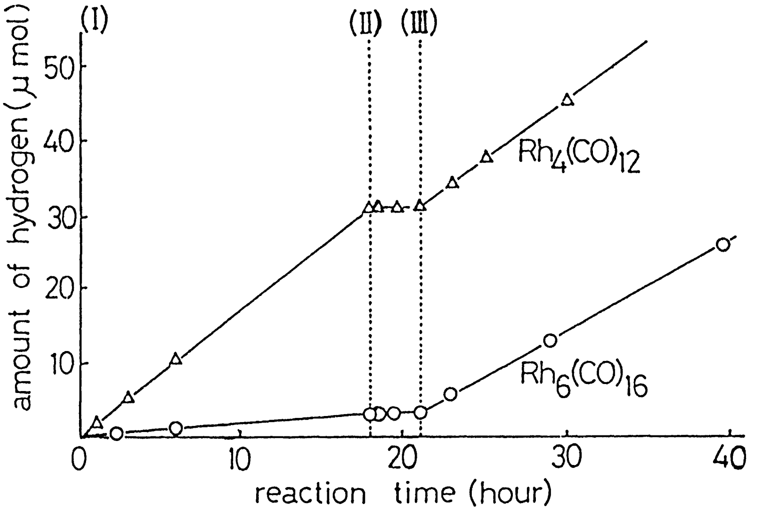

Fig.3. Effect of NO addition to $CO-H_2O$ reaction by aqueous soln. of Rh clusters at 20°C.
complex = $2.0x10^{-5}$ mol in 100ml (KOH=0.89 M)
(I)2.7 mmol of CO was introduced.
(II)After 18h, 0.34 mmol of NO was added to (I).
(II)~(III)NH_3, N_2O and N_2 were formed.
(III)Gaseous NO was consumed at this point.

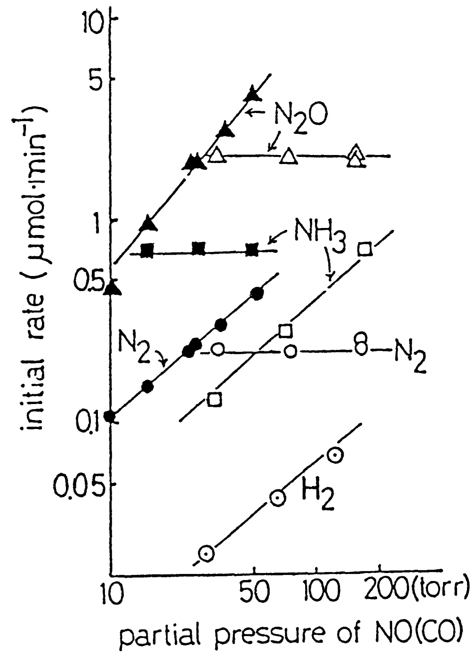

Fig.4. Dependence of the initial rates of the product formatiom upon the partial pressure of NO and CO at 20°C. $Rh_6(CO)_{16}$= $2.4x10^{-5}$mol in 100 ml (KOH=0.89 M)
closed symbol ;dependence of $P_{NO}(P_{CO}$=160 Torr.)
open symbol ;dependence of $P_{CO}(P_{NO}$= 24 Torr.)
⊙ ; dependence of P_{CO} in WGSR (KOH=5.4 M)

the rate of hydrogen formation was followed. After 18 hours, nitric oxide was added to these systems and the change of the reaction rate was investigated. The rate of WGSR in the case of $Rh_4(CO)_{12}$ complex was one order of magnitude faster than the case of $Rh_6(CO)_{16}$ complex before the introduction of nitric oxide. Hydrogen formation stopped completely by the addition of NO, and NH_3, N_2O and N_2 were produced in a similar manner to fig. 1. After gaseous NO was consumed, H_2 began to be formed again, but this time there was not so much difference in the rate of these two complexes. This suggests that by the addition of NO, $Rh_6(CO)_{16}$ complex becomes more active for WGSR, probably because of the transformation of the cluster structure similar to Rh_4 complex.

The dependence of the initial rates upon the partial pressure of NO and CO and also upon the concentration of $Rh_6(CO)_{16}$ complex was investigated at low concentration of KOH (0.89 M), as shown in fig. 4. The rate of each product formation can be expressed apparently as follows; $V_{N_2O} = k_1 P_{NO}^{1.5} P_{CO}^{0} (Rh)^1$, $V_{N_2} = k_2 P_{NO}^{1} P_{CO}^{0} (Rh)^1$, $V_{NH_3} = k_3 P_{NO}^{0} P_{CO}^{1} (Rh)^1$, and in the case of WGSR in the same system, $V_{H_2} = k_4 P_{CO}^{1} (Rh)^1$. The turnover frequency of WGSR obtained in this study of aqueous alkaline solution ($\sim 10^{-5}$ sec^{-1} at 20°C) is much larger than that in the case of ethoxyethanol solution reported in the literature ($\sim 10^{-5}$ sec^{-1} at 100°C)7). We also investigated WGSR by $Rh_6(CO)_{16}$ complex in ethoxyethanol solution at room temperature and found that TOF in ethoxyethanol was more than one order of magnitude lower than that in aqueous solution. These kinetic results also suggest the incorporation of WGSR to the reduction of nitric oxide to form ammonia. The real catalytically active species in these reaction are now under investigation by some spectroscopic methods.

References

1) C.D.Meyer and R.Eisenberg, J.Am.Chem.Soc., 1976, 98, 1364.
2) M.Kubota, K.J.Evans, C.A.Koentger and J.C.Marsters,Jr., J.Am.Chem.Soc., 1978, 100, 342 : J.Mol.Catal., 1980, 7, 481.
3) S.Naito, J.Chem.Soc. Chem.Comm., 1978, 175.
4) M.D.Oates and J.H.Lunsford, J.Mol.Catal., 1980, 9, 91.
5) C-H,Cheng, D.H.Hendriksen and R.Eisenberg, J.Am.Chem.Soc., 1977, 2791.
6) R.B.King, C.C.Frazier, R.M.Hanes and A.D.King,Jr., J.Am.Chem.Soc.,1977,100,2925.
7) C.Ungerman, V.Landis, S.A.Moya, H.Cohen, H.Walker, R.G.Peason, R.G.Rinker and P.C.Ford, J.Am.Chem.Soc., 1979, 101, 5922.
8) H.Kang, C.H.Mauldin, T.Cole and R.Pettit, J.Am.Chem.Soc., 1977, 99, 8323.
9) K.Cann, T.Cole, W.Slegeir and R.Pettit, J.Am.Chem.Soc., 1978, 100, 3969.

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