

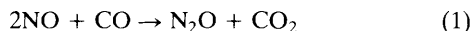
Catalytic Reduction of Nitric Oxide by Carbon Monoxide in the Presence of Platinum(II), Copper(I), and Copper(II)

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Rapid reductions of NO to N₂O by CO can be achieved at ambient temperature in aqueous solution containing K₂PtCl₄, CuCl, CuCl₂, HCl, and LiCl: the average rates for the N₂O and CO₂ evolution are 30.5 and 38.1 turnovers per hour over the first 10 hours.

The reduction of nitric oxide by carbon monoxide, reaction (1), mediated by metal complexes has attracted great attention recently due to its relevance to the control of air pollution and the intrinsic interest in the mechanism of N₂O and CO₂ formation.¹⁻⁷ While a number of catalyst systems for reaction (1) have been reported, only the Rh^{III}-Rh^I and the PdCl₂-CuCl₂ systems rapidly catalyse the reaction and have been investigated in detail. In addition to the catalysis of reaction (1), palladium-copper systems have been useful catalysts in many important reactions,^{4,8} but the analogous platinum-copper system has never found application in any catalytic reaction. We now report the use of K₂PtCl₄-CuCl₂-CuCl as a catalyst system for reaction (1). This system is not only much more active than those previously reported, but also reveals a catalytic mechanism different from the palladium-copper catalysed reactions.



An effective catalyst solution for reaction (1) was prepared by dissolving K₂PtCl₄ (0.100 mmol), CuCl₂ (8.98 mmol), CuCl (4.53 mmol), and LiCl (25.1 mmol) in a mixture of water (98.0

ml) and hydrochloric acid (2.00 ml, 12.1 M). The solution was placed in a 3 l vessel which was evacuated and then charged with NO and CO gases to an initial partial pressure of 500 and 250 Torr, respectively. Quantitative analyses of the gas components over the stirred solution during the course of catalysis were performed according to previous methods.^{3,9} The results shown in Figure 1 indicate that the conversion of NO to N₂O and CO to CO₂ at room temperature proceeded at average rates of 30.5 and 38.1 turnovers/h, respectively, over the first 10 h with no change in activity on recharging. Thus, the present catalyst is approximately 5 and 20 times more active than the PdCl₂-CuCl₂⁴ and Rh^{III}-Rh^I^{3b} systems, respectively. As observed previously,^{3b,4} the N₂O produced (Figure 1) accounts for only ~80% of the NO consumed indicating that not all the NO is converted to N₂O. However, attempts to detect other possible reduced products such as NH₂OH and NH₃ failed.

In order to explore the essential features and requirements of the catalyst system, a number of experiments were performed leading to the following results. (i) No catalysis occurs if either K₂PtCl₄ or CuCl is absent. (ii) In the absence of CuCl₂, N₂O and CO₂ production decreases gradually,

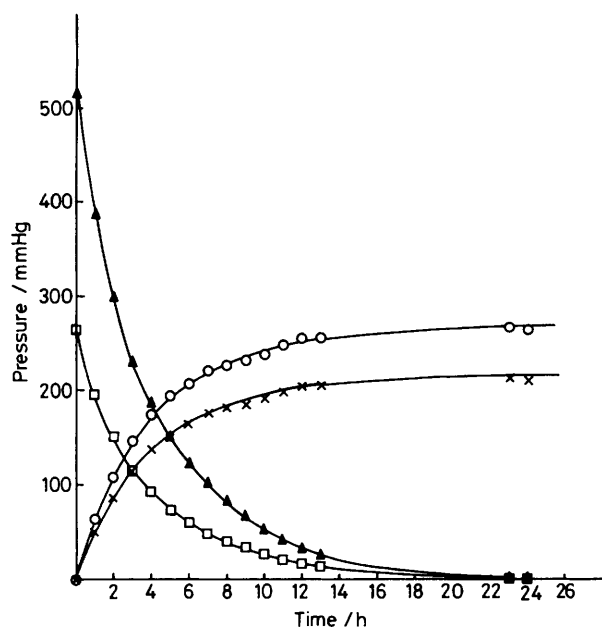


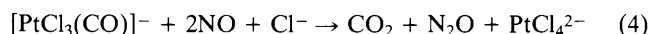
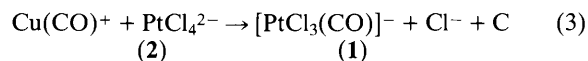
Figure 1. The change in gas composition as a function of time for the catalysis of reaction (1) by the $\text{K}_2\text{PtCl}_4\text{-CuCl-CuCl}_2\text{-HCl-LiCl}$ system; carbon monoxide (\square), carbon dioxide (\circ), nitric oxide (\blacktriangle), and nitrous oxide (\times).

resulting in the formation of an inactive brown platinum carbonyl¹⁰ which is readily converted back to an active solution on the addition of CuCl_2 . (iii) A high concentration of Cl^- increases the solubility of CuCl , but inhibits the catalysis, e.g., at 0.24 M HCl -0.25 M LiCl the N_2O and CO_2 production is 2.5 times faster than at 0.24 M HCl -2.00 M LiCl . (iv) K_2PtCl_4 catalyses the oxidation of CO to CO_2 by CuCl_2 and also catalyses the reduction of NO to N_2O by CuCl , but the rates are only 1/19.8 and 1/8.9 of the CO_2 and N_2O evolutions, respectively, in the catalysis of equation (1). The results clearly indicate that the production of N_2O and CO_2 is greatly enhanced if both NO and CO are present in the catalyst system. It is noteworthy that in the palladium-copper system, the conversions of CO to CO_2 and NO to N_2O are not appreciably affected by the existence of the other reactant gas NO and CO , respectively.⁴

During the course of catalysis, the platinum species observed was $[\text{PtCl}_3(\text{CO})]^-$ (**1**) which may be isolated as $[\text{AsPh}_4][\text{PtCl}_3(\text{CO})]$ by quenching the solution with AsPh_4Cl .^{11†} The formation of (**1**) in the solution is closely related to the ability of Cu^+ as a CO carrier. In one experiment, K_2PtCl_4 in water was added to a $\text{CuCl-CuCl}_2\text{-HCl-LiCl}$ solution which had been saturated with 250 Torr of CO . PtCl_4^{2-} (**2**) anion was completely converted to (**1**) within 5 min as shown by the u.v.-visible spectrum of the solution.‡ The same reaction in the absence of CuCl did not produce (**1**) after 2 h. Presumably, (**1**) is produced by CO transfer from $\text{Cu}(\text{CO})^+$, formed from CO absorption by Cu^+ ion,¹² reactions (2) and (3). Thus, it is clear that the lack of activity of the platinum system in the absence of CuCl [observation (i)] is a consequence of the inability to form (**1**).

† Satisfactory elemental analyses were obtained for $(\text{AsPh}_4)[\text{PtCl}_3(\text{CO})]$. The platinum anion exhibits ν_{CO} at 2082 cm^{-1} (KBr) or 2118 cm^{-1} (H_2O) which is in agreement with the reported ν_{CO} for $\text{CsPtCl}_3(\text{CO})$ (see ref. 11).

‡ PtCl_4^{2-} absorbs at 390 and 480 nm while $[\text{PtCl}_3(\text{CO})]^-$ absorbs at 366 and 420 nm.



The reaction of (**1**) with CO in the $\text{CuCl-CuCl}_2\text{-HCl-LiCl}$ solution gives only a trace of CO_2 in 30 min. However, CO_2 evolution from (**1**) in the same solution is greatly accelerated under NO atmosphere yielding 0.93 equiv. of CO_2 as well as 0.72 equiv. of N_2O within 30 min. A u.v.-visible spectral study indicates that (**1**) is converted to (**2**) in the reaction.‡ Based on these observations, the stoichiometry of the reaction of (**1**) with NO can be established as summarized in reaction (4). These results, together with the fact that (**2**) is readily converted to (**1**) in the presence of $\text{Cu}(\text{CO})^+$ provide a mechanism, reactions (2)–(4), for the fast N_2O and CO_2 formation from the catalyst solution. Moreover, the mechanism explains the observations that fast N_2O and CO_2 evolution occurs only when both NO and CO are present, observation (iv).

From observation (ii), it is clear that Cu^{2+} also serves to oxidize platinum carbonyl to Pt^{2+} in the catalysis. This result coupled with observation (iv) seems to indicate that a minor pathway involving the redox reactions of $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Pt}^{2+}/\text{Pt}^0$ couples, similar to the one proposed for the $\text{PdCl}_2\text{-CuCl}_2$ system⁴ cannot be excluded. However, it should account for less than 6% of the total activity of the observed catalysis as shown by observation (iv).

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References

- B. F. G. Johnson and S. Bhaduri, *J. Chem. Soc., Chem. Commun.*, 1973, 650; S. Bhaduri, B. F. G. Johnson, C. J. Savory, J. A. Segal, and R. H. Walter, *ibid.*, 1974, 809; S. Bhaduri and B. F. G. Johnson, *Transition Met. Chem.*, 1978, 3, 156.
- B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, 1974, **96**, 3325; J. A. Kaduk, T. H. Tulip, J. R. Budge, and J. A. Ibers, *J. Mol. Catal.*, 1981, **12**, 239.
- (a) J. Reed and R. Eisenberg, *Science*, 1974, **184**, 568; (b) C. D. Meyer and R. Eisenberg, *J. Am. Chem. Soc.*, 1976, **98**, 1364.
- M. Kubota, K. J. Evans, C. A. Koerntgen, and J. C. Marsters, Jr., *J. Am. Chem. Soc.*, 1978, **100**, 342; M. Kubota, K. J. Evans, C. A. Koerntgen, and J. C. Marsters, Jr., *J. Mol. Catal.*, 1980, **7**, 481.
- C. S. Chin, M. S. Sennett, P. J. Wier, and L. Vaska, *Inorg. Chim. Acta*, 1978, **31**, L443.
- Y. A. Dorfman, V. S. Emel'yanova, and B. O. Zhusupbekov, *Kinet. Katal.*, 1981, **22**, 375.
- W. P. Fang and C. H. Cheng, *J. Chem. Soc., Chem. Commun.*, 1986, 503.
- J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, and H. Kojer, *Angew. Chem.*, 1959, **71**, 176; J. K. Kochi, 'Organometallic Mechanisms and Catalysis,' Academic Press, New York, 1978, pp. 114–116; R. F. Heck, *J. Am. Chem. Soc.*, 1968, **90**, 5538, 5546; D. E. James and J. K. Stille, *ibid.*, 1976, **98**, 1810.
- C. H. Cheng and R. Eisenberg, *J. Am. Chem. Soc.*, 1978, **100**, 5968.
- J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni, and S. Martinengo, *J. Am. Chem. Soc.*, 1974, **96**, 2614.
- M. J. Cleare and W. P. Griffith, *J. Chem. Soc., A*, 1969, 372; D. B. Dell'Amico and F. Calderazzo, *Inorg. Chem.*, 1984, **23**, 3030.
- M. A. Busch and T. C. Franklin, *Inorg. Chem.*, 1979, **18**, 521, and references therein.