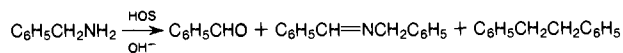


been described: C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963). The need for vacuum-line techniques and the explosive nature of HNF_2 apparently discouraged development of this very interesting reaction. (b) A. Nickon and A. S. Hill (*J. Am. Chem. Soc.*, **86**, 1152 (1964)) showed that sulfonamides of primary amines give alkanes and arenes by treatment with 8–58 mol of hydroxylamine-O-sulfonic acid in boiling strongly basic aqueous systems. Also, *N,N*-disulfonimides, derived from unhindered amines, provide alkanes upon displacement with hydride anions at 150 °C: R. O. Hutchins, F. Cistone, B. Goldsmith, and P. Heuman, *J. Org. Chem.*, **40**, 2018 (1975).

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Benzylhydrazine under similar conditions still gives the normal product—toluene—with a small amount of bibenzyl, suggesting that in the presence of Cu^{2+} benzylhydrazine is not an important intermediate.

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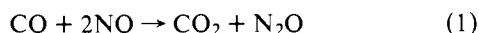
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Reduction of Nitric Oxide by Carbon Monoxide in the Presence of Aqueous Palladium(II) and Copper(II)

Sir:

While highly favored thermodynamically, the reduction



of nitric oxide by carbon monoxide does not proceed even at 450 °C.¹ Heterogeneous systems (metals and their oxides) are used for catalysis of this reaction, but typically elevated temperatures (400 °C) are required.¹ Homogeneous catalysis of reaction 1 at 23 °C has been recently reported by Eisenberg and co-workers.² The only system investigated in depth thus far employs the rhodium(I)–rhodium(III) couple.² The objective of our study is to determine first whether other transition metals may be used for homogeneous catalysis of the NO–CO reaction at room temperature and whether new insights on pathways for this reaction may be derived from these studies. Herein we report the utilization of the palladium(0)–palladium(II) system coupled with the copper(II)–copper(I) system, analogous to the Wacker system, for the catalysis of reaction 1 at room temperature.

The reactions of NO (350 Torr) and CO (360 Torr) in a 125-mL reaction vessel containing 25 mL of aqueous solutions of PdCl_2 , CuCl_2 , or CuCl and 2.0 M HCl were studied using a dual column Varian Aerograph A-350-B gas chromatograph. The yields of CO_2 and N_2O are given in Table I. A molecular sieves 5A column was used to separate the reactants CO and NO and a column packed with Poropak Q was used to separate the products N_2O and CO_2 .

Under conditions comparable with those previously employed, a 3-L sample of a CO–NO mixture over a stirred 10^{-2} M PdCl_2 –0.20 M CuCl_2 –2.0 M HCl (100 mL) solution resulted in conversion of CO to CO_2 at a more rapid rate than the Rh systems previously employed.^{2a} No induction time was observed for formation of CO_2 and N_2O as was observed with the RhCl_3 and RhCl_3 –HCl systems.^{2a} The rate of N_2O formation was faster with the present PdCl_2 – CuCl_2 –HCl system

Table I. Yield of Nitrous Oxide and Carbon Dioxide from Reaction of NO and CO at 25 °C^a

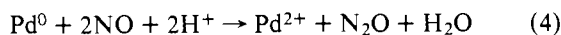
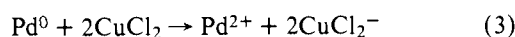
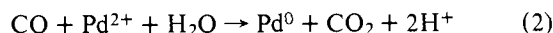
Run	PdCl_2 , M	Copper(II) or copper(I), ^b M	N_2O		CO_2 , yield, %
			Torr	Yield, %	
1	0.010		152	76	88
2	0.010	0.20	140	75	100
3	0.100	0.20	151	80	100 ^c
4	0.010	0.20	140	75	100 ^c
5	10^{-3}	0.20	88	47	99 ^c
6	10^{-4}	0.20	48	26	100 ^c
7	10^{-3}	0.002	19	11	9.1
8	10^{-3}	0.020	41	23	29.4
9	10^{-3}	0.200	94	50	90
10	10^{-3}	0.600	47	25	100
11	10^{-3}	1.00	37	21	100
12	10^{-3}	2.00	23	13	100
13	10^{-3}	10^{-3} ^b	17	10	8.4
14	10^{-3}	0.010 ^b	29	16	15.0
15	10^{-3}	0.100 ^b	80	45	41
16	10^{-3}	1.00 ^b	129	72	70

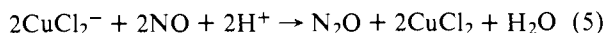
^a Reaction time, 24 h. ^b Concentration of CuCl_2^- . ^c Reaction, 18 h.

than the rates previously reported for the RhCl_3 and RhCl_3 –HCl systems, but slower than the system employing $\text{Rh}(\text{CO})_2\text{Cl}_2^-$ catalyst.^{2a} Experiments designed to elucidate aspects and significant species involved in the reaction are summarized in Table I.

Aqueous PdCl_2 (run 1) was shown to effect conversion of CO–NO to CO_2 and N_2O , but the rate of reaction was eventually decreased as metallic palladium was deposited. In the absence of CO there was negligible N_2O formation from the systems containing NO– PdCl_2 –HCl and NO– PdCl_2 – CuCl_2 –HCl. Precipitation of palladium(0) can be obviated in the presence of CuCl_2 –HCl (run 2) with formation of soluble CuCl_2^- and oxidation of palladium(0). Conversion turnovers of up to 120 mol of N_2O /mol of palladium(II) were observed. The rate and yield of N_2O formation were increased with increasing palladium(II) concentration (runs 3–6). The rate of N_2O formation was first order with respect to partial pressure of NO, but the kinetic orders with respect to palladium(II) and copper(II) appear to be complex functions which are still under investigation. The yield of N_2O formation was unchanged with variation of HCl concentration at 4, 3, 2 and 1 M. At HCl concentrations lower than 1 M the rate of N_2O formation was greatly reduced with precipitation of CuCl and palladium(0). With H^+ maintained at 2 M (using HClO_4), the optimum yield of N_2O was obtained with 2.6 M Cl^- . The use of 0.20 M CuBr_2 –2.0 M HBr gave a reduced N_2O yield (21%) compared with 47% obtained with the corresponding chloride solution. The N_2O yield was found to increase with increasing CuCl_2 concentration (0.002–0.200 M), but high concentrations of CuCl_2 gave lower yields of N_2O (runs 7–12). The typical Wacker conditions (0.03 M PdCl_2 , 2.2 M CuCl_2 , 3.3 M LiCl) gave lower N_2O yields than those shown in Table I. Solutions containing CuCl could be used instead of CuCl_2 and the yield of N_2O formation was enhanced by higher concentrations of CuCl_2^- (run 13–16). The yield of N_2O (17%) from the reaction of NO with 0.20 M CuCl_2^- –2.0 M HCl, which was slightly less in the presence of CO, was increased to 55% for the reaction of NO with 1.0×10^{-3} M PdCl_2 –0.20 M CuCl_2^- –2.0 M HCl. The presence of CO does not appreciably alter the rate of N_2O formation in the latter system.

The reactions leading to conversion of CO and NO to CO_2 and N_2O include





The oxidation of CO by Pd^{2+} (reaction 2) which is first order³ with respect to CO, Pd^{2+} , and Cl^- , is more rapid than the N_2O forming reactions 4 and 5. The reaction of NO with CuCl_2^- is relatively slow,⁴ but the rate of this reaction is considerably enhanced in the presence of Pd^{2+} . A palladium(II)-copper(I) chloride bridged species may be the reactive entity for reaction with NO, analogous to the tin(II)-copper(I) species suggested for the rapid copper(I) catalyzed reduction of NO with tin(II).⁴ A UV-visible spectral study of the NO-CO-PdCl₂-CuCl₂ systems reveals the formation of a new band at 450 nm which we attribute to such a palladium(II)-copper(I)-NO species. This absorption band which is also observed in an aqueous solution containing PdCl₂-CuCl-NO-HCl decays with concomitant growth in intensity of absorption due to copper(II) at 800 nm. Palladium forms nitrosyl complexes such as Pd(NO)₂Cl₂ and insoluble PdNOCl, the latter which reacts with HCl to give N₂O, palladium(0) and palladium(II).⁵ Under the present experimental conditions, the reaction of PdCl₂ with NO leading to PdNOCl and subsequent N₂O formation was found to be unimportant. The reaction of NO with a mixture of 50.0 mg of palladium(0) in 2 M HCl gave only a small yield of N₂O (5%) after stirring for 72 h. The results thus far appear to be consistent with a suggestion that the reactive entities for N₂O production are chloride bridged species containing palladium(II)-copper(I) and palladium(II)-palladium(0). The reduced rate of N₂O formation at high copper(II) concentration may be due to reduced palladium(0) concentrations (reaction 3) or formation of a copper(II)-NO complex⁶ which, however, is unstable in aqueous solutions. The decreased rate of NO consumption at high copper(II) concentrations indicates that metal-NO complex formation is not an important factor.

Preliminary infrared spectral studies of the aqueous PdCl₂-CuCl₂-NO-CO systems have not provided useful results thus far. It would be appropriate at this stage to propose that a significant intermediate in the N₂O forming reaction is likely to be a palladium hyponitrite species with a cis-bidentate oxygen-bonded hyponitrite ligand such as reported for the complex resulting from the reaction of NO with the platinum(0) complex Pt(PPh₃)₃.⁷ Further studies are being pursued to elucidate the mechanisms of reactions in the CO-NO-PdCl₂-CuCl₂ system and to seek even more efficient systems for the CO-NO reaction.

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Nitroxide. 84.

Copper(II)-Bisnitroxide Complex as Evidence for Strong Electron-Exchange Six-Spin System

Sir:

ML_n type transition metal complexes in which L^- is a paramagnetic ligand and M^{n+} a metal ion can give information on electronic interactions.¹⁻⁸

If M^{n+} is diamagnetic, this system is analogous to an organic polyradical.^{9,10} If M^{n+} is paramagnetic, in a doublet state for instance, supplementary interactions are expected, leading to different electron spin resonance (ESR) spectra. ESR spectra of compounds containing several paramagnetic centers can be interpreted according to Schlichter's formalism.^{9,11-14} For a ML_2 system, the spin hamiltonian can be represented by the six-spin diagram shown in Chart I, where a_M is the hyperfine interaction between the unpaired electron spin and the metal nuclear spin I_M ,¹⁵ a_N is the hyperfine interaction between the unpaired electron and one nuclear spin I_N in the ligand,¹⁶ g_M and g_L are the corresponding g factors, and J and J' are the exchange interactions.

If dipolar interactions are small enough, the ESR spectrum in fluid isotropic solution of such a species will depend upon the relative magnitude of the absolute value of J and J' with respect to the absolute value of the hyperfine interactions and to $\Delta g = |g_M - g_L|$ in appropriate units.

Simple spectra are obtained in two limiting cases. In the weak exchange case, $|J|$ and $|J'|$ are both much smaller than $|a_M|$, $|a_N|$, and $|\Delta g\beta H|$ (β Bohr magneton, H applied magnetic induction); the spectrum is the superposition of the spectra of the isolated species. In the strong exchange case, ($|J|$ and $|J'| \gg |a_M|$, $|a_N|$, and $|\Delta g\beta H|$), one expects a signal centered at $g = (g_M + 2g_L)/3$, composed of $(2I_M + 1)(4I_N + 1)$ peaks, the splitting between lines being reduced to $a_M/3$ and $a_N/3$.

A simple example is to be found in complexes of Cu^{2+} ($I_{\text{Cu}} = 3/2$) with ligands containing nitroxide free radicals ($g_L \approx 2.006$, $I_N = 1$, $a_N \approx 15$ G). Although several examples of this type are known,^{1,2,5-7} with g -value evidence for strong exchange,^{1,6,7} to our knowledge no example has been reported

Chart I

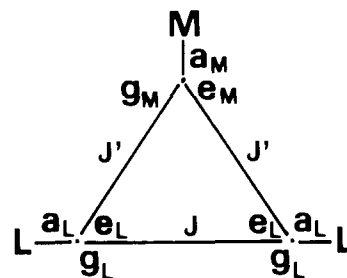
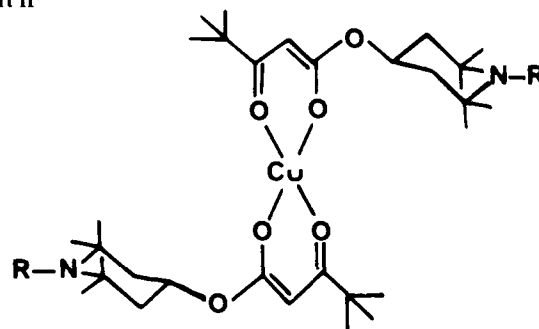


Chart II



1 R = H

2 R = O