

Preliminary results with chelated Fe^{III} and H_2O_2 indicate the formation of hydroxyl radicals (see Table I).

Similar experiments were performed with 0.05 M 2- and 3-POBN and 0.05 M sodium persulfate for comparison with 4-POBN. The hydroxy adduct of 3-POBN gives a spectrum wherein the hfsc from the hydroxy proton is barely resolved: $a_{\text{N}} = 14.94$, $a_{\beta}^{\text{H}} = 1.60$, $a_{\gamma}^{\text{H}} = 0.26$ G at 0.08 G modulation amplitude (0.26-G line width). The spectrum obtained from 2-POBN consists only of a triplet of doublets: $a_{\text{N}} = 15.39$, $a_{\beta}^{\text{H}} = 2.25$ G (0.77-G line width). As such it cannot be assigned to the hydroxy spin adduct at this time.

Acknowledgment. This work was supported by the National Research Council of Canada. Grateful acknowledgment is hereby made.

References and Notes

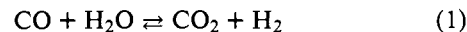
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- (7) Unpublished spectra obtained from various sources by B. J. Blackburn and J. I.-P. Liu; some experiments have been repeated recently and the same spectra recorded but satisfactory proof of assignment could not be obtained.
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- (9) α -4-Pyridyl 1-oxide *N*-*tert*-butyl nitron was made from 4-pyridinecarboxaldehyde 1-oxide and *tert*-butylhydroxylamine, mp 181-183 °C. The aldehyde was obtained from MnO_2 oxidation of 4-pyridylcarbinol 1-oxide. The latter was made from $\text{H}_2\text{O}_2/\text{HOAc}$ oxygenation of commercially available 4-pyridylcarbinol. Similar methods were used to prepare the 3 and 2 isomers, mp 127-128 and 88-90 °C, respectively. NMR, mass spectra, IR, UV, and C, H, N are in agreement with the structures assigned.
- (10) Protons attached to oxygen or nitrogen but not to carbon are rapidly exchanged in D_2O in nitroxide spin adducts.
- (11) Electron transfer to produce 4-POBN $^+$ could give the hydroxy adduct by reaction with water. The same could come from hydrolysis of the sulfate adduct.
- (12) The fact that the hfsc's are substantially different in these two pH ranges suggests that the protonated adduct may be intramolecularly hydrogen bonded. One type of spin adduct which is intramolecularly hydrogen bonded has been previously detected (E. G. Janzen and I. G. Lopp, *J. Magn. Reson.*, **7**, 107 (1972)).

Edward G. Janzen,* Y. Y. Wang, Raghav V. Shetty
Guelph Waterloo Centre for Graduate Work in Chemistry
Department of Chemistry, University of Guelph
Guelph, Ontario, N1G 2W1
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Active Homogeneous Catalysts for the Water Gas Shift Reaction Derived from the Simple Mononuclear Carbonyls of Iron, Chromium, Molybdenum, and Tungsten

Sir:

A reaction of carbon monoxide of obvious importance in the use of coal as a clean energy source is the so-called water gas shift reaction



Recent papers have reported systems for the homogeneous catalysis of this reaction based on ruthenium¹ and rhodium² carbonyl derivatives. This paper describes the homogeneous catalysis of the water gas shift reaction using basic solutions of the mononuclear metal carbonyls $\text{Fe}(\text{CO})_5$ and $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$).

Some typical experiments using metal carbonyls as catalyst precursors for the water gas shift reaction are summarized in Table I. The indicated quantities of the metal carbonyl and base were added to the indicated solvent in a 700-mL stainless steel reaction vessel. After closing the reaction vessel, CO was added to the specified pressure. The reaction vessel was heated and held at the indicated constant temperature for one or more days. Gas samples were periodically withdrawn and analyzed by vapor phase chromatography on a 1/4 in. \times 6 ft 5A molecular sieve column calibrated with known H_2/CO mixtures. To check for internal consistency occasional samples were analyzed for CO_2 on a silica column.

The results summarized in Table I indicate that a variety of mononuclear metal carbonyls in basic solutions have considerable activity for the catalysis of the water gas shift reaction. In these reactions the presence of the base appears to be essential since runs in the absence of added base produce little or no hydrogen (runs 5 and 14). The combination of $\text{Mo}(\text{CO})_6$ with KBH_4 in methanol (run 13) shows comparable catalytic activity to $\text{Mo}(\text{CO})_6$ with KOH in the same solvent (runs 7-9) but at much lower base/metal ratios.

In some cases with $\text{Mo}(\text{CO})_6$, the reaction vessel contained dark solids suspended in a yellowish liquid at the end of the reaction. To exclude the possibility of this catalysis being heterogeneous, i.e., arising from these precipitated solids rather than the homogeneous supernatant liquid, the individual catalytic activities of both the precipitated solid and the supernatant solution remaining in the reaction vessel after conclusion of a reaction were checked. The precipitated solids were filtered off and added to a fresh solution of methanol and aqueous base (run 9a). The catalytic activity of the resulting suspension was relatively small. In contrast the supernatant solution when repressurized with CO exhibited essentially the same catalytic activity as before (run 7a). Thus the catalytically active species appears to be in the supernatant solution rather than in the precipitated solids indicating a homogeneous rather than heterogeneous mode of catalysis for this reaction.

Identification of the various metal carbonyl species present in the reaction solutions under catalytic conditions was attempted by recording their infrared spectra using a stainless steel high pressure infrared cell with Irtran I windows.^{3,4} For example, $\text{Fe}(\text{CO})_5$ (0.10 mL, 0.15 g, 0.76 mmol; measured $\nu(\text{CO})$ in 1:20 water-1-butanol: 2020 (sh), 1996 (vs) cm^{-1}) was dissolved in a nitrogen-saturated solution of 0.12 g (3 mmol) of sodium hydroxide in 1.4 mL of water and 48 mL of 1-butanol. The infrared spectrum of the solution exhibited bands at 1915 (s, sh), 1885 (vs), and 1865 (sh) cm^{-1} indicating the expected^{5,6} conversion of $\text{Fe}(\text{CO})_5$ to $\text{HFe}(\text{CO})_4^-$ by the base (reported⁷ $\nu(\text{CO})$ of $\text{HFe}(\text{CO})_4^-$ in dimethylformamide: 2008 (w), 1914 (m), 1880 (s) cm^{-1}). This solution of $\text{HFe}(\text{CO})_4^-$ was then pressurized with 330 atm of CO in the

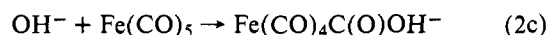
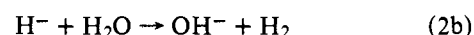
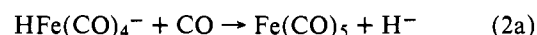
Table I. Systems Derived from the Mononuclear Metal Carbonyls as Catalysts for the Water Gas Shift Reaction^a

Run	Metal Carbonyl	Base	Solvent	Initial CO pressure, atm	Metal concn, M	Base/metal mol ratio	Temp °C	mol of H ₂ /mol of metal per day
1	Fe(CO) ₅	NaOH	<i>n</i> -BuOH	28.2	0.0112	28	137	16
2	Fe(CO) ₅	NaOH	<i>n</i> -BuOH	28.2	0.0112	28	164	52
3	Fe(CO) ₅	NaOH	<i>n</i> -BuOH	28.2	0.0112	28	181	72
4	Fe(CO) ₅	NaOH	<i>n</i> -BuOH	14.1	0.0112	28	161	200
5	Fe(CO) ₅	None	<i>n</i> -BuOH	23.1	0.0112	0	150	~0.01
6	Cr(CO) ₆	KOH	MeOH	7.8	0.00182	1100	140	280
7	Mo(CO) ₆	KOH	MeOH	4.3	0.00731	53	125	40
							135	115
7a	Filtrate of reaction mixture from run 7						125	24
8	Mo(CO) ₆	KOH	MeOH	4.3	0.00207	87	125	22
							120	5
9	Mo(CO) ₆	KOH	MeOH	4.3	0.0022	760	140	24
							115	9
							135	10
							160	40
9a	Solids precipitating from the reaction mixture during run 9 + MeOH + KOH						150	26
10	Mo(CO) ₆	KOH	MeOH	11	0.00208	800	155	4
							120	0
							130	3
							145	130
11	Mo(CO) ₆	KOH	<i>n</i> -BuOH	11	0.0026	650	140	31
12	Mo(CO) ₆	KOH	THF	11	0.00208	800	160	11
13	Mo(CO) ₆	KBH ₄	MeOH	4.3	0.0036	3	105	1
							120	5
							140	30
14	Mo(CO) ₆	none	MeOH	4.3	.00255	0	160	0
15	W(CO) ₆	KOH	MeOH	7.7	0.00132	1265	95	0
							110	13
							130	140
16	W(CO) ₆	KOH	MeOH	7.7	0.00177	111	155	460 ^b
17	W(CO) ₆	KOH	MeOH	7.7	0.00105	1600	170	~900 ^d
^c	Ru ₃ (CO) ₁₂	KOH	EtOCH ₂ CH ₂ OH	1	0.0006	17	100	1.2
^c	Ru ₃ (CO) ₁₂	KOH	MeOH	48	0.0001	40	110	37.5

^a For runs 1–5 170 mL of *n*-BuOH and 30 mL of 2.08 M aqueous NaOH were used. For runs 6–17 100 mL of solvent was used. When KOH is indicated, this was added as a 10 M aqueous solution. ^b In this run over a 16-h period 2.77 mol of hydrogen was obtained for each mol of KOH. Therefore the reaction is catalytic in KOH. ^c Data from R. M. Laine, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 252 (1977). ^d Corresponds to consumption of >65% of the carbon monoxide originally introduced.

high pressure infrared cell and its infrared spectrum was measured periodically. No change in the infrared spectrum of the solution was noticed upon standing for 4 h at room temperature under 330 atm of CO. However, upon gradual heating under CO pressure, the characteristic strong 1885-cm⁻¹ band of HFe(CO)₄⁻ gradually disappeared with the concurrent appearance of a 1995-cm⁻¹ band indicating the presence of regenerated Fe(CO)₅. In this experiment with a base/Fe(CO)₅ ratio of 3.9 the formation of Fe(CO)₅ from HFe(CO)₄⁻ and 330 atm of CO was complete at 93–98 °C. Increasing the base concentration increased the temperature necessary to react all of the HFe(CO)₄⁻ to Fe(CO)₅ at a given CO pressure. For example, with a base/Fe(CO)₅ ratio of 9.2 the formation of Fe(CO)₅ from HFe(CO)₄⁻ and 330 atm of CO was complete only at 104–109 °C. Furthermore at temperatures above 125 °C under 330 atm of CO a new ν(CO) frequency began to appear at 2300 cm⁻¹ which may be assigned to CO₂ produced in the water gas shift reaction. Cooling these mixtures to room temperature in the high pressure infrared cell resulted in partial regeneration of HFe(CO)₄⁻ from reaction of Fe(CO)₅ with residual base, even when the CO pressure was maintained. No evidence for the formation of the known^{8,9} formyl derivative HC(O)Fe(CO)₄⁻ was observed in any of these experiments.

These infrared spectroscopic studies at high CO pressures indicate that CO can displace the hydride ligand from HFe(CO)₄⁻ to form Fe(CO)₅. This suggests the following cycle for the catalysis of the water gas shift reaction by iron carbonyl:

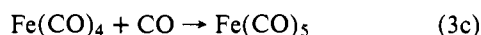
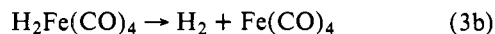
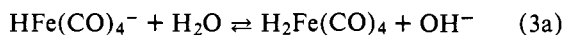


Equation 2b corresponds to the well-known vigorous reactions of ionic hydrides (e.g., NaH) with water to give hydrogen and hydroxide.¹⁰ The nucleophilic attack of a metal-bonded carbonyl group with hydroxide to give a metal-bonded carboxyl group (eq 2c) is well established in metal carbonyl cation chemistry^{11,12} and has reasonable experimental support in the rhodium carbonyl catalyzed water gas shift reaction.² Carboxyl groups directly bonded to transition metals similar to that in the proposed intermediate Fe(CO)₄C(O)OH⁻ are well known^{12–14} to undergo facile decarboxylation to give the corresponding metal hydride exactly as in eq 2d. The sum of 2a–d is the water gas shift reaction.

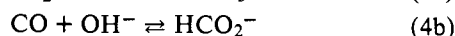
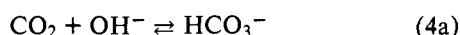
Additional evidence for the validity of step 2a was obtained by monitoring the changes in the infrared spectrum upon heating a solution of [(C₆H₅)₃P]₂N⁺HFe(CO)₄⁻ in anhydrous tetrahydrofuran under 330 atm of CO. Conversion of HFe(CO)₄⁻ into Fe(CO)₅ under these conditions was complete at 60 °C. Upon cooling the solution to room temperature while maintaining the CO pressure some of the Fe(CO)₅ reverted to HFe(CO)₄⁻. More of the Fe(CO)₅ reverted to HFe(CO)₄⁻ as the CO pressure was lowered in stages. How-

ever, below ~140 atm the conversion became quite rapid with the formation of $\text{HFe}(\text{CO})_4^-$ being complete within minutes. These observations imply that step 2a can be written as an equilibrium when anhydrous nonhydroxylic solvents are used.

An alternative mechanism for the iron carbonyl catalyzed water gas shift reaction involves the participation of $\text{H}_2\text{Fe}(\text{CO})_4$. The key steps for hydrogen evolution are shown in Eq 3a-c (which are possible substitutes for 2a + 2b in the mechanism given above):



A detailed study of the effects of CO pressure and base concentration on the rates of H_2 and CO_2 evolution for the iron carbonyl catalyzed reaction should allow identification of the operative mechanism, but the existence of the equilibria 4a and 4b complicate interpretation to the degree that the data at hand are insufficient for a definitive mechanistic assignment.



Similarly, with the $\text{Mo}(\text{CO})_6/\text{KBH}_4$ system the possibility exists that $\text{HMo}_2(\text{CO})_{10}^-$ may be an intermediate in the reaction scheme. The anions $\text{HM}_2(\text{CO})_{10}^-$ have been shown¹⁵ to form in reactions of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo},$ and W) with BH_4^- in donor solvents at elevated temperatures.

Despite the mechanistic ambiguities still remaining, our work clearly indicates that the range of metal carbonyls which can be used as catalyst precursors for the water gas shift reaction is far greater than that suggested by previous results.^{1,2} In particular, carbonyls of relatively inexpensive metals such as chromium, molybdenum, tungsten, and iron as well as those of rare and expensive metals such as ruthenium¹ and rhodium² can give catalytically active systems for this important reaction.

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- Postdoctoral research associate, 1976-1978.
- Postdoctoral research associate, 1976-1977.

R. B. King, C. C. Frazier,¹⁶ R. M. Hanes,¹⁷ A. D. King, Jr.*
Department of Chemistry, University of Georgia
Athens, Georgia 30602

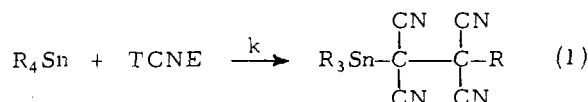
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Photoassisted Intermolecular Charge-Transfer Processes for Organometals: Insertion of Tetracyanoethylene and Spin Adducts with Quinones

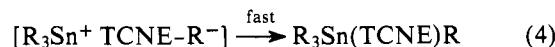
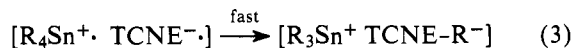
Sir:

Organometals can react readily with a variety of compounds under mild conditions to produce paramagnetic intermediates as a result of charge-transfer interactions in which the organometal functions as the donor. We wish to show that the same process can be introduced photochemically by irradiation of the charge-transfer band at low temperatures, or with organometals in which the thermal reactions do not occur.

The addition of TCNE to various tetraalkyllead and -tin compounds results in a transient charge-transfer spectrum, the disappearance of which coincides with the formation of 1,2 adducts (eq 1), which have been well characterized.¹ From the

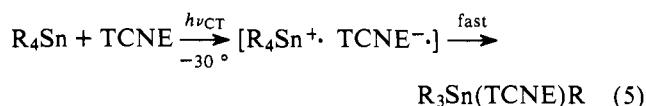


structural effects on kinetics and selectivities it was shown that the thermal addition occurred by the following mechanism:



The rate-limiting step in eq 2 is an electron-transfer process which accords with the linear relationship observed between $\log k$ and λ_{max} of the charge-transfer band as well as the ionization potentials of the organometals.¹ Thus, for the family of group 4b alkyl metals, the rates of insertion decrease precipitously in the order: $\text{PbEt}_4 \gg \text{SnEt}_4 \gg \text{GeEt}_4 > \text{SiEt}_4$, as a result of the rising trend in their ionization potentials from 8.13, 9.01, 9.40 to 9.78 eV, respectively.

If this mechanism is correct, the direct irradiation of the charge-transfer band should also promote the same insertion reaction in eq 1 except at lower temperatures. Indeed, we now find that the process in eq 1 can be carried out photochemically by the irradiation at the charge-transfer band under conditions in which the thermal reaction is too slow. For example, the charge-transfer band of the Et_4Sn -tetracyanoethylene (TCNE) complex occurs at 426 nm, and the half-life for disappearance is ~6 h at 30 °C. At -30 °C the charge-transfer complex is stable and no addition occurs within 2 h. However, irradiation with a 100-W medium-pressure Hg lamp at 426 nm (using a Jarrell-Ash 82-410 monochromator) affords a 50% yield of the same adduct within this period:



Similar results have been obtained with Me_4Sn , in which the addition to TCNE in eq 1 proceeds with second-order kinetics when carried out thermally. The temperature dependence of the second-order rate constant k shows an activation energy of $\Delta H^\ddagger = 13 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -41 \text{ eu}$, for this addition. In marked contrast, the rate of the photochemically induced addition is unchanged between -30 to +20 °C, when the concentration of the reactants and the light intensity are held constant. The related compounds Et_4Ge and Et_4Si do not undergo significant insertion of TCNE thermally at 30 °C. However, TCNE adducts similar to those in eq 1 can be ob-