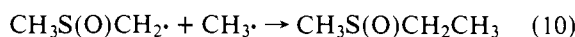
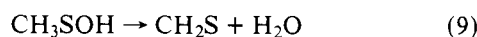
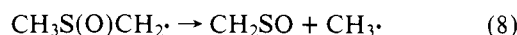
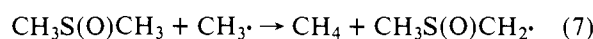
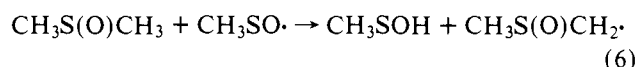


to be a source of methanesulfenic acid at 500–650 °C. We have previously established the formation of sulfine in the FVP of dimethyl sulfoxide<sup>8</sup> and can readily amend our mechanism to account for formation of the sulfenic acid via a hydrogen atom abstraction step (eq 6) or less likely by way of ethyl methyl sulfoxide (eq 10, 11) which we also find to be a thermal source of methanesulfenic acid. Thioformaldehyde is also detected in the pyrolysis of dimethyl sulfoxide at 600–800 °C and presumably arises from dehydration of methanesulfenic acid. It is clear that dimethyl sulfoxide, in addition to being a key organosulfur reagent and valuable solvent with an extensive chemistry<sup>2a,14</sup> is also a remarkably rich thermal source of reactive molecules. Yet another thermal source of methanesulfenic acid is allyl methyl sulfoxide, which affords both the sulfenic acid and sulfine at temperatures above 250 °C. It is likely that allyl methyl sulfoxide decomposes by a radical mechanism similar to that indicated in eq 5–8 (a competing retro-ene<sup>1b</sup> route to sulfine cannot be excluded).



Microwave spectroscopic study of the thermolysis products of several isotopic modifications of *tert*-butyl methyl sulfoxide allows spectral assignments to be made for the <sup>13</sup>C, <sup>34</sup>S, <sup>18</sup>O, hydroxy-*d*<sub>1</sub>, methyl-*d*<sub>3</sub>, and methyl-*d*<sub>3</sub> <sup>34</sup>S modifications of methanesulfenic acid.<sup>15</sup> These and the normal species assignments result in the following “substitution” structure for methanesulfenic acid: C–S = 1.806 (2) Å, S–O = 1.658 (2) Å, O–H = 0.957 (10) Å, ∠CSO = 100.1 (1)°, ∠SOH = 107.7 (4)°, dihedral angle (displacement from “eclipsed” *cis*) ∠CSOH = 93.9 (1)°; dipole moment = 1.87 (7) D.<sup>17,19</sup> Methanesulfenic acid has thus been found to contain dicoordinate rather than tricoordinate sulfur (form A rather than B, eq 1); we find no evidence for the presence of the isomeric form of methanesulfenic acid containing tricoordinate sulfur with hydrogen bonded to sulfur.

A number of overall rotational transitions are found to be split into “quartets” by the internal rotation of the methyl and hydroxyl groups. Analysis of these splittings gives a 2.4 (1) kcal mol<sup>-1</sup> threefold potential barrier to internal rotation about the C–S bond and 5.4 (2) and 4.1 (2) kcal mol<sup>-1</sup> *cis* and *trans* potential barriers to internal rotation about the S–O bond. Compared with the internal rotation in H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>S<sub>2</sub>, the hindering potential for rotation about the S–O bond in methanesulfenic acid bears much more resemblance to the latter.<sup>20</sup> The half-life of methanesulfenic acid in the gas phase at 0.1 Torr and 25 °C is ~1 min. We shall report elsewhere on a photoelectron spectroscopic study of methanesulfenic acid.

**Acknowledgment.** Support for this research from the Research Corporation (R.E.P.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (E.B.), and the University of Missouri—St. Louis is gratefully acknowledged. We thank Professor Frank Davis for informing us of his results prior to publication and Professor Saul Wolfe for helpful discussions.

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## Catalysis of Carbon Monoxide Hydrogenation by Soluble Mononuclear Complexes

Sir:

We report the homogeneous hydrogenation of carbon monoxide to methanol, higher primary alcohols, and their formate esters in the presence of soluble, mononuclear catalysts. In the course of an investigation of the proposed<sup>1</sup> free-radical mechanism for the cobalt-carbonyl catalyzed homogeneous hydrogenation of arenes, we decided to verify the predicted slow reduction of benzene. Accordingly, 160 mL of

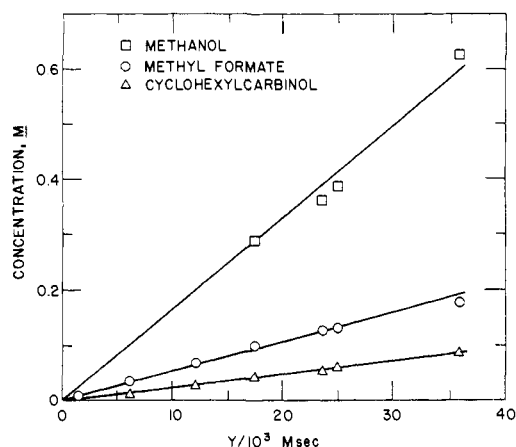


Figure 1. Growth of the major reaction products in the system  $\text{CO}/\text{H}_2/\text{C}_6\text{H}_6/\text{CO}_2(\text{CO})_8$  at 200 °C (300 atm).

benzene (AR grade) containing 8 mmol of freshly sublimed  $\text{CO}_2(\text{CO})_8$  was heated to 200 °C in a clean,<sup>2a</sup> stirred autoclave (nominal capacity 300 mL) in the presence of 300 atm of an equimolar mixture of  $\text{H}_2$  and  $\text{CO}$  ("synthesis gas"). Samples (seven) were taken from the liquid phase over a period of 1 week for analysis. After each sampling the pressure was restored by means of a double-piston compressor.<sup>2b</sup> Each sample was analyzed colorimetrically for total cobalt,<sup>3,4</sup> by methylene blue titrimetry for  $\text{HCo}(\text{CO})_4$ ,<sup>5</sup> the principal cobalt species in these solutions, and by flame ionization GLC for organic products.<sup>6</sup> Reduction products of benzene<sup>7a</sup> were found (e.g., the concentration of cyclohexylcarbinol increased linearly with the variable  $y \equiv \int_0^t [\text{HCo}(\text{CO})_4] dt$ , as expected<sup>1</sup> for a reaction which is first order in hydride), but additional peaks in the chromatograms were also observed to grow in even faster (Figure 1). The two principal unexpected products were identified as methanol and methyl formate, with pseudo-first-order formation rate constants  $k$ , defined by  $d[\text{X}]/dt \equiv k[\text{HCo}(\text{CO})_4]$ , equal to  $1.6 \times 10^{-5} \text{ s}^{-1}$  and  $5.6 \times 10^{-6} \text{ s}^{-1}$ , respectively. The minor products detected were ethanol, ethyl formate, and 1-propanol. At least ten turnovers<sup>8</sup> of the catalyst with respect to  $\text{CO}$  hydrogenation products were achieved during the time the solutions retained their color (yellow-brown), homogeneity, and clarity.<sup>9</sup> Blank runs conducted in an identical fashion except for the omission of either dicobalt octacarbonyl or hydrogen resulted in no detectable production of either methanol or methyl formate ( $<1 \times 10^{-5} \text{ M}$ ).

To ascertain that the alcohols and their esters originated from  $\text{CO}$  hydrogenation and were independent of benzene hydrogenation, experiments were conducted with heptane and *p*-dioxane as solvents. In heptane at 200 °C, methanol and methyl formate were produced five–ten times more slowly. In *p*-dioxane at 182 °C, carbon monoxide hydrogenation proceeded more cleanly and rapidly (Figure 2); it is evident from the curvature of the plots in Figure 2 that ethanol and 1-propanol are products of secondary reactions of methanol.<sup>20</sup> The constancy of the ratios of alcohols to corresponding formates suggested that the transesterification reactions are rapid. Thus, the rate of formation of total products is regarded as a measure of the rate of hydrogenation of  $\text{CO}$ . The pseudo-first-order rate constants for formation of total products in two separate experiments at 196 °C with initial  $\text{HCo}(\text{CO})_4$  concentrations of 24 and 47 mM were  $(3.46 \pm 0.24) \times 10^{-5} \text{ s}^{-1}$  and  $(4.00 \pm 0.08) \times 10^{-5} \text{ s}^{-1}$ , respectively. Because these determinations do not differ at a statistically significant level, we conclude that the principal rate-determining path is first order in the soluble mononuclear species,  $\text{HCo}(\text{CO})_4$ , and that catalysis by cobalt atom clusters or precipitated metal is at most a minor path.

Our surprise at the evident hydrogenation of carbon mon-

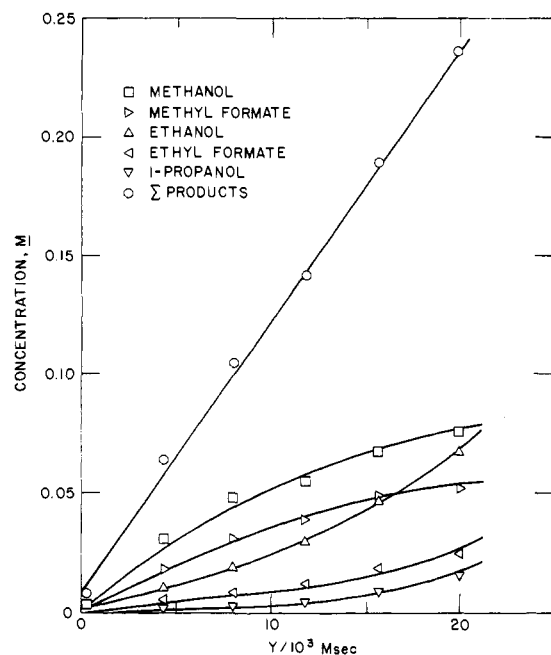
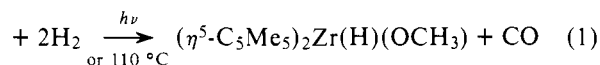
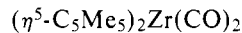


Figure 2. Growth of the major  $\text{CO}$  hydrogenation products in the system  $\text{CO}/\text{H}_2/p\text{-dioxane}/\text{CO}_2(\text{CO})_8$  at 182 °C (300 atm).

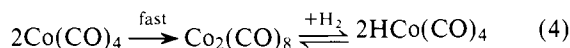
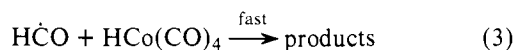
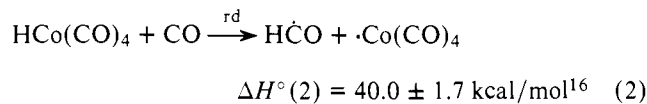
oxide was based on statements<sup>10a,b</sup> that no mononuclear compound had been shown to function as catalyst for the hydrogenation of the very strong triple bonds in dinitrogen or carbon monoxide. Muetterties and coworkers<sup>10c</sup> examined a large number of classic mononuclear coordination catalysts in the  $\text{H}_2 + \text{CO}$  reaction with a wide range of solvents (but at much lower temperatures and pressures) and had found none to be active; he has suggested<sup>10b</sup> that triple bonds in  $\text{CO}$  and isoelectronic molecules may be optimally activated toward catalytic reduction by the bond-stretching and -weakening effects of coordination to multiple metal centers. The utility of metal clusters as catalysts for  $\text{CO}$  hydrogenation is undoubted. Thus,  $\text{Os}_3(\text{CO})_{12}$  or  $\text{Ir}_4(\text{CO})_{12}$  in toluene solution have been found<sup>10c</sup> to be mildly catalytic for reduction of  $\text{CO}$  to  $\text{CH}_4$ , and the latter<sup>10d</sup> also yields ethane in a  $\text{NaAlCl}_4$  melt at 180 °C. Likewise, Walker et al.<sup>11</sup> reported salts of the cluster anion  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  in THF or dioxane to be active for hydrogen reduction of  $\text{CO}$  to methanol, ethylene glycol, glycerol, and propylene glycol. (Note that the formation of methane by photolysis of  $\text{HCCO}_3(\text{CO})_9$  under synthesis gas arises from the apical  $\text{CH}$  group and not from hydrogenation of carbon monoxide.<sup>12</sup>)

The only reported reduction by hydrogen of carbon monoxide coordinated to an unequivocal mononuclear complex is that of Bercau et al.<sup>13</sup>



The reduced complex yields methanol on acid hydrolysis; this process is, however, stoichiometric and not catalytic. Two other reports bear on catalysis of  $\text{CO}$  hydrogenation by mononuclear complexes. Gresham<sup>14</sup> patented a process for the preparation of ethylene glycol, glycerol, and their formate esters from synthesis gas at 184–242 °C and a pressure of 3000 atm, the catalyst precursor being cobaltous acetate. It is likely, but not certain, that the active catalyst in this process is  $\text{HCo}(\text{CO})_4$ . On the other hand, in those patents<sup>15a-c</sup> which claim the formation of methanol and polyhydric alcohols from synthesis gas, weak bases, salts, and mononuclear rhodium starting materials, such as  $\text{Rh}(\text{CO})_2(\text{acac})$ , catalysis may be associated with a hydridocarbonyl rhodium cluster compound.<sup>15d</sup>

Based on paired experiments in benzene (200, 220 °C) and *p*-dioxane (182, 196 °C), the apparent activation enthalpy for formation of CO hydrogenation products is  $40.7 \pm 6\%$  kcal/mol. This result is compatible with a strongly endothermic rate-determining (rd) step (eq 2) in which hydrogen atom transfer to CO yields formyl and cobalt tetracarbonyl radical pairs in a manner entirely analogous to the proposed<sup>1</sup> arene hydrogenation mechanism. Where this mechanism applies, triple-bond hydrogenation need not make use of cluster catalysts; prior hydrogen atom transfer is sufficiently bond weakening to cause the moiety to be susceptible to further reduction. Furthermore, if the H atom transfer mechanism is valid other complexes, capable of reversible hydrogen activation by reaction analogous to eq 4 and possessing metal-hydrogen bonds not too much stronger than that in  $\text{HCo}(\text{CO})_4$  (58 kcal/mol),<sup>16a</sup> should also be capable of CO hydrogenation. This prediction was successfully tested with the system  $\text{Mn}_2(\text{CO})_{10}$ - $\text{HMn}(\text{CO})_5$  in *p*-dioxane. The total manganese content was 0.2 or 0.6 M, the temperature was 240 °C, and the partial pressures of CO and  $\text{H}_2$  were 102 and 204 atm, respectively. These conditions were chosen on the basis of the successful use of  $\text{HMn}(\text{CO})_5$  for arene hydrogenation<sup>7a</sup> by the H atom transfer-radical pair mechanism,<sup>7b</sup> an estimate for  $D(\text{HMn}(\text{CO})_5)$  of  $64 \pm 1$  kcal/mol, the greater stability of  $\text{HMn}(\text{CO})_5$  than of  $\text{HCo}(\text{CO})_4$  toward loss of CO,<sup>19c</sup> and the less favorable equilibrium constant for the analogue of eq 4. Pseudo-first-order rate constants for the formation of methanol and total product were found to be  $1.3 \times 10^{-5} \text{ s}^{-1}$  and  $1.4_6 \times 10^{-5} \text{ s}^{-1}$ , respectively, and proportionality between hydrogenation rate and concentration of  $\text{HMn}(\text{CO})_5$ <sup>17</sup> was observed.



Further mechanistic speculations<sup>18</sup> based on the available data would not be warranted. Efforts to ascertain the probable reaction pathway(s) via variations of temperature, pressure, solvent, catalyst concentration, and by appropriate labeling studies are underway.

The homogeneous, catalytic formation of methanol from synthesis gas by mononuclear catalysts which is now reported was unexpected because it had been so long overlooked in the very extensive review literature<sup>19</sup> of such systems. The further observation that the same catalyst system simultaneously converts methanol to higher alcohols, probably via the "homologation" reaction of alcohols,<sup>20</sup> opens the way to a detailed study of the long-sought homogeneous analogues of both the Fischer-Tropsch and methanol synthesis catalysts.

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- (17) Concentrations of  $\text{HMn}(\text{CO})_5$  were determined by a titrimetric procedure similar to that used for  $\text{HCo}(\text{CO})_4$ .
- (18) A referee has raised the question as to whether the ethylene glycol production reported in Gresham's patent<sup>14</sup> may have arisen from dimerization of the formyl radicals which we would presume to be present at significantly higher steady-state concentrations at 225–250 °C and 3000-atm pressure. We believe this to be a reasonable possibility and are examining the evidence.
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## Alkali Metal Ion Specificity in the Solution Ordering of a Nucleotide, 5'-Guanosine Monophosphate

Sir:

The 5'-guanosine monophosphate dianion (5'-GMP) was recently reported to form a regular ordered structure in aqueous solution that is slow to exchange on the <sup>1</sup>H NMR time scale.<sup>1</sup> The most informative evidence for structure formation was provided by the presence of four nonequivalent H(8) resonances in the limiting spectrum of the disodium salt in D<sub>2</sub>O solution near 0 °C. The large chemical shift range for the H(8) protons (1.3 ppm) and the appearance of nonequivalent amino proton lines indicated that both base stacking and hydrogen bonding are important in the self-structuring processes. Based on these observations and consideration of infrared frequency shifts in the carbonyl stretching region, it was concluded that structure formation arises from limited stacking of planar tetramer units (I) formed by hydrogen bonding between positions N(1) and N(2) as donors and O(6) and N(7) as acceptors.<sup>2</sup>

The slow chemical exchange of self-assembled 5'-GMP is