total system. Schuster's model apparently considers that this separation is large, and the reaction essentially follows curve 1 to the intersection and then curve 2. If changes in the oxidation potential of D result simply in vertical displacements of curve 2, this will indeed lead to $\alpha < 1$, with, to the extent that the curves may be considered linear in the region of intersection, a constant value.

The alternative approach assumes less separation and emphasizes the splitting of energy levels which occurs on crossover between two states of similar energy. Here the reaction should really follow the lower dotted curve between 1 and 2. Charge transfer is neither rate determining nor complete in the transition state, but its extent increases along the reaction coordinate to the products, A.[9]

This formulation suggests a very similar transition state for reactions leading to other quite different (transient) products, B and C. The reaction to C is simply a nucleophilic displacement by D on the peroxide bond, with an early, polarized transition state, while B represents a possible low-energy path for radical production.[10] The energy levels indicated for A, B, and C are arbitrary and will depend on the structures of RO–OR and D. In fact, more than one may be formed, or they may equilibrate, even within the original solvent cage.

How then can we hope to describe more exactly the reaction paths followed in these reactions? Product studies, including fast spectroscopic determination of transient intermediates, should distinguish reactions leading to A, B, or C. Here, Schuster has convincing evidence for (eventual) electron transfer to yield $D^{+\cdot}$ in some cases, and free radicals are sometimes detected.[11] However, in most systems, the observed products are most easily accounted for as the consequences of simple initial nucleophilic displacement.[12] Probing transition-state structures is more difficult, since "complete" and "partial" charge-transfer formulations lead to qualitatively similar predictions. Investigation of steric effects on rates should give some indication of the "tightness" or extent of bond formation in the transition state, and here an early study of benzoyl peroxide–phenol reactions has shown that ortho substitution markedly slows rates.[13] Similarly, several isotope labeling studies have shown that the carbonyl oxygen of acyl peroxides largely or completely retains its identity in reactions with amines,[14] phenols,[14] and electron-rich double bonds,[15] a result at least consistent with incipient bond formation in the transition state.

If reactions leading to A-, B-, and C-type products in fact occur through transition states of significantly different structure, one would expect them to show significantly different changes in rate with structure and other reaction conditions. As far as I know, this has not been demonstrated.[16]

(9) Although electron transfer from donor to peroxide is strongly endothermic as indicated, electron transfer from electron-rich aromatics to an acyloxy radical is exothermic, so curves 1 and 2 cross. Thus, electron-rich aromatics may be electrolytically oxidized in the presence of carboxyylate anions; cf.: Sasaki, K.; Newby, W. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, *20*, 137–165. Stated another way, increased electron density weakens RO–OR bonds. The rate of decomposition of benzoyl peroxides shows a negative Hammett ρ value: Swain, C. G.; Stockmeyer, W. H.; Clarke, J. T. *J. Am. Chem. Soc.* **1950**, *72*, 5426–5434.

(10) A fourth process to simply yield D + 2RO· can be ruled out, since the back-reaction 2RO· → ROOR may be presumed to have negligible activation energy. Accordingly, the barrier to peroxide decomposition can only be lowered by coupling with some other process such as electron transfer or covalent bond formation.

(11) For example, the reaction of *m*-chlorobenzoyl peroxide and *p,p'*-dimethoxystilbene gives 10% scavengeable radicals: Greene, F. D.; Adam, W.; Cantrill, J. E. *J. Am. Chem. Soc.* **1961**, *83*, 3461–3468.

(12) Thus, aromatics commonly undergo acyloxy substitution, although the possibility that this arises from fast recombination of fragments from path A cannot be excluded.

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(14) Denney, D. B.; Denney, D. Z. *J. Am. Chem. Soc.* **1960**, *82*, 1389–1393.

(15) Greene, F. D. *J. Am. Chem. Soc.* **1959**, *81*, 1503–1506.

(16) Although I have emphasized reactions of peroxides, a similar attempt to evaluate the significance of electron transfer in reactions between organometallic compounds and halogens etc. has been made by Kochi, e.g.: Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141–2152.

Acknowledgment. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

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Hydrogenation of Carbon Monoxide to Methanol and Ethylene Glycol by Homogeneous Ruthenium Catalysts

Sir:

Conversion of synthesis gas—a feedstock derivable from many sources—to organic chemicals has become a very important goal within the chemical industry as world petroleum prices continue to rise. Homogeneous catalysis will serve a significant function in this framework if highly selective processes operative at low pressures can be developed. Although there are recent reports of homogeneously catalyzed CO hydrogenation at low pressures, rather low rates of product formation were observed.[1-3] Other published work in this area has been limited to high pressures, generally above 1000 atmospheres (atm). The first demonstration that organic products (including ethylene glycol and glycerine) could be obtained from H_2/CO by homogeneous catalysis was performed with cobalt catalysts under extreme pressures (1500–5000 atm).[4] Subsequently, rhodium catalysts were found to be catalytically active at elevated pressures, especially for conversion of synthesis gas to ethylene glycol,[5] and continued research on this system has given improved results at lower pressures.[6] Recently, a number of homogeneous catalysts (based on iron, ruthenium, and iridium) have been reported to hydrogenate carbon monoxide to ethylene glycol and/or methanol at pressures substantially above 1000 atm.[7-9] In contrast to these reports of catalysis under extreme conditions, we present here some initial studies of ruthenium catalysts at pressures of 340 atm and below, including the observation of homogeneous CO hydrogenation under moderate conditions, and a remarkable promoter effect of carboxylic acids on the formation of ethylene glycol by these catalysts. Since the completion of our original manuscript, essentially identical observations have appeared in a patent application.[10]

Reaction of acetic acid solutions of $Ru_3(CO)_{12}$ with mixtures of CO and H_2 at pressures above ca. 100 atm produces substantial quantities of methyl acetate and smaller amounts of ethylene glycol diacetate, as shown in Table I. Traces of glyercine triacetate have also been detected in these mixtures.[11] Significant obser-

(1) (a) Thomas, M. G.; Beier, B. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 1296. (b) Demitras, G. C.; Muetterties, E. L. *Ibid.* **1977**, *99*, 2796.

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(6) For example, see: Kaplan, L. (to Union Carbide Corp.) U.S. Patent 4162261, 1979, in which experiments at pressures below 550 atm are described.

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(8) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419.

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(10) Knifton, J. F. (to Texaco Development Corp.) UK Pat. Appl. 2024811, 1980.

(11) In addition to these products, ethyl acetate is also formed in reactions done in acetic acid. The ethanol is apparently derived largely from acetic acid by catalytic hydrogenation, since reactions in propionic acid solvent yield similar quantities of propyl propionate and only traces of ethyl propionate.

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Table I. Hydrogenation of Carbon Monoxide with Ruthenium Catalysts[a]

reaction	solvent	mmol of CH_3O–	mmol of –OCH_2CH_2O–
1	50 mL of acetic acid	52.2	1.37
2	50 mL of propionic acid	61.0	1.03
3	50 mL of acetic acid[b]	14.9	0.41
4	50 mL of acetic acid[c]	139	1.58
5	40 mL of acetic acid, 10 mL of H_2O	66.8	0.75
6	40 mL of acetic acid, 10 mL of cyclohexane	39.7	0.82
7	40 mL of acetic acid, 10 mL of THF	45.9	1.03
8	40 mL of acetic acid, 10 g of H_3PO_4	48.2	0.21
9	50 mL of THF	19.4	
10	50 mL of ethyl acetate	33.1	
11	50 mL of ethanol	55.6	
12	50 mL of ethanol[c]	109	

[a] All reactions were performed in a glass-lined rocker bomb with 2.35 mmol of Ru [charged as $Ru_3(CO)_{12}$], at 230 °C under 340 atm of 1:1 H_2/CO for 2 h, unless noted otherwise. [b] 0.70 mmol of Ru charged. [c] Reaction at 260 °C.

vations concerning the character of the catalyst in this solvent are (a) infrared spectra of reaction solutions immediately after depressurization show a high concentration of $Ru(CO)_5$; (b) after exposing these solutions to light and ambient conditions for a period of hours, the ruthenium charged can be recovered essentially quantitatively as $Ru_3(CO)_{12}$; (c) high-pressure infrared spectra under reaction conditions (400 atm of 1:1 H_2/CO, 200 °C) show $Ru(CO)_5$ and no $Ru_3(CO)_{12}$;[12] (d) many ruthenium complexes, including $H_4Ru_4(CO)_{12}$,[13] $[Ru(CO)_2(CH_3CO_2)_2]_n$,[14] $Ru_6C(CO)_{17}$,[15] $H_3Ru_3(CO)_9(CCH_3)$,[16] and $Ru(acac)_3$, are equivalent catalyst precursors [equal rates to products result, and the ruthenium can be recovered as $Ru_3(CO)_{12}$]; (e) no plating of ruthenium metal is observed in these reactions until temperatures above ca. 265 °C (at 340 atm) are reached;[17] and (f) first-order rate dependences of glycol and methanol formation on ruthenium concentration are observed (for example, compare reactions 1 and 3 in Table I). These observations strongly suggest that the catalyst in this reaction is a soluble, mononuclear carbonyl complex, as proposed independently for a ruthenium-catalyzed reaction in which synthesis gas is converted to one-carbon products at higher pressures.[8]

Experiments to determine how ethylene glycol is formed in this catalytic system showed that (a) reactions in solvents other than carboxylic acids (e.g., ethers, alcohols, esters, hydrocarbons, etc.) under conditions given in Table I do not produce detectable amounts of ethylene glycol (less than ca. 0.02 mmol), but can give methanol yields nearly equivalent to those observed in acetic acid (cf. reactions 1, 10, and 11 in Table I);[18,19] (b) when Brønsted acids of noncarboxylic nature with a range of acidities are added to these solvents, they do not promote glycol formation, nor do

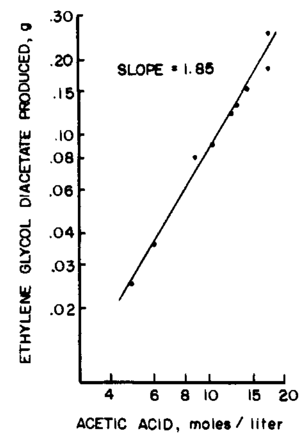


Figure 1. Log-log plot of ethylene glycol diacetate yield vs. acetic acid concentration when diluted with varying amounts of methyl acetate and H_2O. Conditions are specified in Table I.

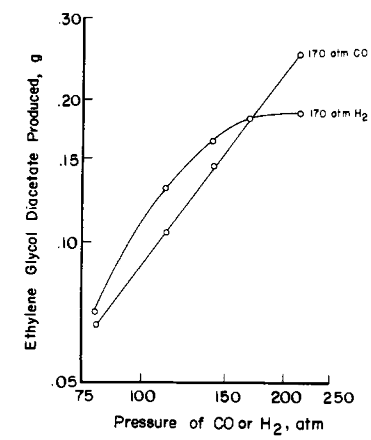
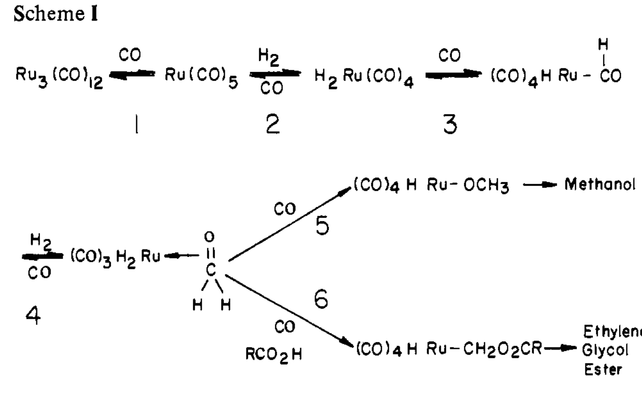


Figure 2. Ethylene glycol diacetate yield as a function of varying CO and H_2 partial pressures, at constant 170 atm H_2 and CO partial pressures, respectively. Other conditions are listed in Table I.

Scheme I



they increase glycol production when added to carboxylic acid solvents; (c) dilution of acetic acid by many inert cosolvents (Table I) causes decreased rates to glycol with little change in methanol rates (see Figure 1, which indicates an approximate dependence of glycol rate on the second power of acetic acid concentration); and (d) a number of carboxylic acid solvents have been investigated, and those which were stable under reaction conditions promoted the formation of glycol esters. Carboxylic acids are thus found to be quite specific promoters for glycol formation, and acidity alone is not a sufficient condition for promoting glycol formation.

Further information on the glycol-producing reaction has been gained by studying the effects of carbon monoxide and hydrogen partial pressures (Figure 2). The dependence of glycol rate on CO pressure is large at low pressure, but approaches zero order at higher CO levels. This change in order is perhaps related to the shifting equilibrium between $Ru_3(CO)_{12}$ and mononuclear,

(12) At 200 °C and pressures of 1:1 H_2/CO below about 200 atm, a mixture of $Ru_3(CO)_{12}$ and $Ru(CO)_5$ is detected.

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(16) Canty, A. J.; Johnson, B. F. G.; Lewis, J.; Norton, J. R. J. Chem. Soc., Chem. Commun. 1972, 1331.

(17) Removable glass liners are used; plating of ruthenium metal, when it occurs, is obvious not only from its visual appearance but also from the formation of hydrocarbon products in such runs. These products are absent in strictly homogeneous runs. See ref 8 for experiments and discussion related to the question of homogeneous vs. heterogeneous ruthenium catalysis.

(18) Added ethylene glycol was shown to be stable in these mixtures under reaction conditions.

(19) Methyl formate is reported to be a significant product from reaction of H_2/CO with Ru catalysts under higher pressures.[8] We have found only traces of this product at pressures of 340 atm and below.

catalytically active species, which is supported by high-pressure infrared measurements. A dependence on H_2 partial pressure between first and second order (ca. 1.3) is observed, suggesting an equilibrium involving H_2 prior to the rate-determining step. The formation of methanol in these reactions exhibits the same behavior with respect to H_2 and CO partial pressures, and only minor changes in product distribution are observed on changing the gas composition or pressure.

A mechanistic sequence consistent with all of these observations is shown in Scheme I. Reaction of $Ru(CO)_5$ with H_2 has been observed[20] by high-pressure infrared spectroscopy to produce $H_2Ru(CO)_4$ (step 2). Although an isolated example of hydride migration to coordinated CO has not yet been observed, this appears to be a reasonable first step in CO hydrogenation by this system. Reductive elimination of the resultant formyl ligand could yield coordinated formaldehyde (step 4), as previously proposed in a mechanism for the Fisher–Tropsch reaction.[21] Since this catalytic system is highly specific for methanol formation in the absence of carboxylic acids, a methoxy ligand rather than a hydroxymethyl ligand is presumed to be the methanol precursor; the latter might be expected to yield at least traces of longer chain products. Insertion of formaldehyde into a Ru–H bond to give the methoxy ligand (step 5) could presumably occur in both the presence and the absence of carboxylic acids. However, the formation of a metal–carbon-bonded intermediate (step 6) has been written requiring a carboxylic acid to account for the observed effect of these compounds on glycol formation by this system. This step perhaps involves acylation[22] of a coordinated formaldehyde intermediate by a hydrogen-bonded acid dimer or protonated acid molecule, which would be consistent with the observed high dependence of the glycol formation rate on acid concentration[23] (Figure 1). A related osmium complex containing coordinated formaldehyde has been shown to undergo electrophilic attack by $CF_3SO_3CH_3$ at the oxygen atom, yielding a metal–carbon-bonded methoxymethyl product.[25] The analogous acyloxymethyl product formed by step 6 is presumed to be a glycol precursor, leading to glycol esters through successive CO insertion, reductive elimination, and hydrogenation.[26] Model studies with a related manganese acyloxymethyl complex have demonstrated that these steps can occur even under mild conditions.[27] The presence of a longer chain product, glycerine, can also be accounted for by extension of this scheme with a glycolaldehyde (ester) intermediate. Ethylene glycol has been reported to be a product of cobalt-catalyzed reactions under moderate pressures, and a similar scheme for glycol formation was presented.[3]

Overall rates of carbon monoxide hydrogenation in these catalytic reactions (in several types of solvents) are nearly equal to those recently reported for a similar ruthenium system operated at much higher pressure—for example, a rate of 8.3×10^{-3} turnovers s^{-1} was observed in reaction 4, Table I, as compared with a reported[8] rate (to methanol and methyl formate) of 1.05×10^{-2} s^{-1} at 270 °C under 1300 atm in THF solvent. This comparison exhibits the importance of solvent effects in homogeneous catalysis, even when the catalyst is presumably uncharged and mononuclear; rate improvements obtainable by large increases in pressure may also be achieved by appropriate choice of solvents. An even more important role of reactive, carboxylic acid solvents in this system is demonstrated by the discovery that they cause formation of a two-carbon product by a catalyst which otherwise produces only methanol. The function of this unique solvent/promoter is apparently to intercept a catalytic intermediate and change the course of its reaction. Further research based on these results is in progress.

Acknowledgment. I thank T. D. Myers for performing these experiments, Drs. Leonard Kaplan and George O'Connor for support and helpful discussions, and Union Carbide Corporation for permission to publish this work.

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Received June 6, 1980

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(22) Reactions done in solutions of acetic anhydride also produce ethylene glycol diacetate. However, much of the anhydride is hydrogenated under reaction conditions, yielding ethyl acetate and acetic acid.

(23) For example, esterification of alcohols by acetic acid is observed to be second order in acid concentration, and an acid dimer is believed to be involved.[24]

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(27) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466.

Resonance Raman Spectra of (Dioxygen)(porphyrinato)(hindered imidazole)iron(II) Complexes: Implications for Hemoglobin Cooperativity

Sir:

We report $Fe–O_2$ stretching frequencies, determined via resonance Raman (RR) spectroscopy, for oxygenated 1-methyl-, 2-methyl-, and 1,2-dimethylimidazole (1-MeIm, 2-MeIm, and 1,2-diMeIm) adducts of the Fe(II) complex of "picket fence" porphyrin,[1] *meso*-tetrakis[$\alpha,\alpha,\alpha,\alpha$-[(*o*-pivaloyl)amido]phenyl]-porphyrin, $H_2TpivPP$. The solution ν_{Fe-O_2} frequency of the 1-MeIm adduct has previously been shown[2] to differ by only 1 cm^{-1} from that of oxyhemoglobin[3] (O_2Hb, 567 cm^{-1}). This relatively high frequency suggested appreciable $Fe–O_2$ multiple bonding,[2] consistent with the short $Fe–O_2$ bond length, 1.75 Å, obtained from the crystal structure of the 1-MeIm adduct.[4]

A substantially longer $Fe–O_2$ bond, 1.90 Å, has been determined[5] for the 2-MeIm adduct. The 2-methyl group hinders the approach of the 2-MeIm-bound Fe to the porphyrin plane. This ligand was introduced by Collman and Reed[6] to prepare 5-coordinate high-spin Fe(II) porphyrins, analogues of deoxyhemoglobin. Nevertheless, O_2 does bind to the 2-MeIm adduct, but the Fe atom is somewhat out of the plane,[5] away from the O_2, and the 2-MeIm–Fe bond is also slightly stretched, relative to the 1-MeIm–Fe bond.[4]

The structure of the 2-MeIm adduct was determined with crystals in which one ethanol molecule is hydrogen bonded to each 2-MeIm N-1 proton.[5] We have determined the RR spectrum of this material at low temperature, with low laser power levels, in a spinning sample cell, to minimize possible artifacts due to laser heating. At −70 °C, the $Fe–O_2$ frequency was located at 561 cm^{-1}. Under the same conditions, a frequency of 572 cm^{-1} was observed for the 1-MeIm adduct. As the temperature was allowed to rise, these bands broadened and shifted to lower frequency (Figure 1). This temperature effect may be due to the population of multiple $Fe–O_2$ rotational conformations, consistent with the orientational disorder observed in the crystal structures.[4,5] The 1,2-diMeIm adduct, whose structure is not available, gave frequencies similar to those of the 2-MeIm adduct. These results are summarized in Table I.

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(6) Collman, J. P.; Reed, C. A. *J. Am. Soc.* **1973**, *95*, 2048.

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