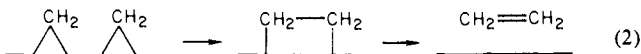


Figure 2. Comparison of four-carbon isomer distributions obtained with $\text{H}_2/\text{CH}_2\text{N}_2$ and H_2/CO over a 39% Co/kieselguhr catalyst at 210 °C and 1-atmosphere pressure.

is the predominant volatile product formed, together with nitrogen.⁸ We conclude that the principal reaction of CH_2 fragments alone on a metal surface is not polymerization but simply dimerization and loss of ethylene from the surface (eq 2).⁹



However, when H_2 is mixed with CH_2N_2 and the gaseous mixture passed over these materials, the nature of the product changes markedly. Over Co, Fe, and Ru, there is produced a mixture of hydrocarbons ranging from 1 to 18 carbons and higher, depending on the conditions (especially temperature and H_2 concentration).¹⁰ The hydrocarbons produced are mainly linear alkanes and monoolefins characteristic of those produced in the Fischer-Tropsch reaction; as the hydrogen partial pressure is increased, the olefin content decreases, and the chain length decreases. Typical distributions are given in Figure 1.

In Figure 2, there is indicated the very close similarity in the distribution of the various four-C hydrocarbons produced from CH_2N_2 and H_2 at 210 °C and 1 atmosphere over a cobalt catalyst and by CO and H_2 over the same cobalt catalyst at 210 °C and 1 atmosphere.

On Ni and Pd surfaces, diazomethane plus H_2 react to produce not only methane but higher hydrocarbons as well (Figure 1) whereas CO and H_2 over the same catalysts at low pressures (1 atmosphere) give mainly CH_4 . However, when CO and H_2 are passed over the Ni catalyst at greater pressures (68 atmospheres)

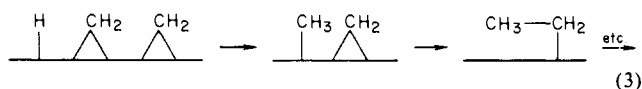
(8) Extraction of the catalyst residues with hot xylene following the reaction with CH_2N_2 frequently led to the isolation of small and varying amounts of "polymethylene" having an IR spectrum similar to polyethylene. This material could arise through polymerization of CH_2 fragments on the surface initiated through the presence of metal-hydride bonds (see text), the latter being produced either in the catalyst preparation or through dissociation of CH_2 groups on the surface to metal carbide and hydride. This point is under further investigation.

(9) Several organometallic species possessing two metal atoms and a CH_2 group have recently been isolated; in each case, when the CH_2 group could conceivably have been bonded either as a bridging methylene unit between two metal atoms or as a carbene unit bonded to one atom, the former arrangement is observed. Such a bonding mode is then suggested for CH_2 fragments on metal surfaces; see: Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* 1980, 102, 1752-1754, and references therein.

(10) In the reaction of diazomethane over an Ru catalyst previously reduced with H_2 , a crystalline white solid was also formed; this was identified as polyethylene by infrared analysis and differential scanning calorimetry, the latter for which we thank Dr. F. Stehling.

higher linear hydrocarbons are produced, and the distribution closely resembles that shown by CH_2N_2 and H_2 over the same catalyst at 1 atmosphere (see Figure 1). Over a copper surface, the $\text{CH}_2\text{N}_2/\text{H}_2$ reaction still gives ethylene as the predominant product just as it does when the reaction is conducted in the absence of hydrogen.

The very close similarities in the hydrocarbon reaction products of CO and H_2 on the one hand and CH_2N_2 on the other over the various transition-metal surfaces suggest a common mechanism for the two processes. The $\text{CH}_2\text{N}_2/\text{H}_2$ reactions indicate that methylene groups do polymerize on these surfaces but that the polymerization is initiated by metal-hydride bonds. Reduction of a methylene group to a methyl group followed by sequential insertion of methylene groups into metal-alkyl bonds is a polymerization mechanism consistent with the data (eq 3).¹¹ Two



termination steps would then be β -hydride elimination of the metal-alkyl to produce an α -olefin and reduction of the metal-alkyl to give an alkane. In the CO/ H_2 reactions, the absorbed methylene species could be produced through reduction of metal-carbide groups following dissociative chemisorption of CO as originally suggested by Fischer and Tropsch.³ In the case of copper, which does not readily dissociatively chemisorb H_2 to form metal-hydride bonds,¹² the initiation step for the oligomerization of the CH_2 species is lacking, and the $\text{CH}_2\text{N}_2/\text{H}_2$ reaction leads only to dimerization and ethylene formation.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the Department of Energy for financial assistance.

(11) Such a chain growth scheme has previously been considered: Biloen, P.; Helle, J. N.; Sachler, W. M. H. *J. Catal.* 1979, 58, 95-107.

(12) Ponec, V.; Knor, Z.; Cerňý, S. *Discuss. Faraday Soc.* 1966, 41, 149-161.

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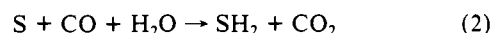
Received March 20, 1980

Homogeneous Catalysts for Utilization of Synthesis Gas as a Reducing Agent

Sir:

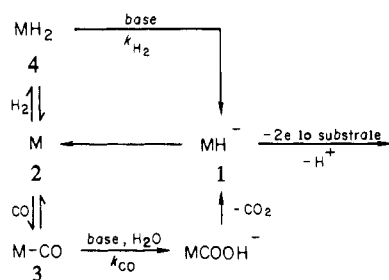
The principal primary product of the gasification of coke with steam and oxygen is a mixture of carbon monoxide and hydrogen of widely varying composition, depending on the conditions used.¹ This mixture, referred to as synthesis gas, is further treated with steam over a metal catalyst to obtain hydrogen for use as a reducing agent, and the CO component of the mixture is converted to CO_2 and H_2 (the water gas shift reaction); the CO_2 is then separated to afford hydrogen.

Catalytic reductions with H_2 are of course well-known (eq 1, S = substrate), and we have recently shown that in certain cases analogous catalytic reductions can be effected with CO and H_2O as the reducing agent² (eq 2).



(1) For example, the Texaco partial oxidation process and the Shell Koppers process produce synthesis gas composition of 1:2 and 2:1 of CO/ H_2 , respectively.

(2) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R. *J. Am. Chem. Soc.* 1978, 100, 3969.

Scheme I. Pathways for Reductions with H₂ and COTable I. Effect of Temperatures on Reductions with Synthesis Gas (600 psi), CO/H₂ = 1.0³

catalyst	substrate	temp, °C	selectivity ratio
Ir ₄ (CO) ₁₂	PhNO ₂	112	0.17
		137	0.23
		162	0.31
		187	0.54
Rh ₆ (CO) ₁₆	PhNO ₂	92	0.57
		112	0.59
		137	0.92
		162	1.2

We report now the development of a homogeneous catalyst system which, for certain reactions, allows for the direct utilization of synthesis gas as the reducing agent, i.e., a simultaneous combination of eq 1 and 2. Furthermore, the reductions can proceed with each component (CO and H₂) in proportion to their initial partial pressures, thus allowing for the direct utilization of any composition of synthesis gas.

The reactions studied are electron-transfer type reductions typified by the reduction of nitroarenes to aminoarenes, and the catalysts employed are metal carbonyls used in conjunction with a base. In the catalytic cycle, it is presumably the anionic metal hydride (1 in Scheme I) which is the principal electron-donating species; with H₂ alone as the reducing agent, 1 is produced by oxidative addition of H₂ to the metal carbonyl species M (2) followed by removal of a proton with the base, whereas when CO is used 1 is formed by basic attack on the metal carbonyl 3 in the aqueous medium followed by loss of CO₂. The two pathways are indicated in Scheme I.

The present objective is to obtain a system which utilizes both paths simultaneously. We find that the various metal carbonyls, which were shown earlier to be effective catalysts for the reduction of nitroarenes to amines with CO as the reducing agent, display widely divergent behavior when H₂ or mixtures of H₂ and CO are used. Thus, Fe(CO)₅ [M = Fe(CO)₄ in Scheme I], while being a very active catalyst for reduction of nitroarenes with CO at 25 °C, is completely inactive at this temperature when H₂ is employed. Os₃(CO)₁₂ is an active catalyst with CO as the reducing agent and is also active with H₂ in the presence of base. It is also found to be an active catalyst when mixtures of CO and H₂ are used, each in excess, but analysis at the end of the reaction indicates that only the CO component of the mixture is used for the reduction. In this instance, the species 2 [i.e., Os₃(CO)₁₁] prefers to undergo coordination with CO rather than oxidative addition to H₂, and the presence of CO thus "poisons" the catalyst as far as the utilization of H₂ is concerned.

However, using 1:1 mixture of CO and H₂ with Ir₄(CO)₁₂ and Rh₆(CO)₁₆ as catalysts, we find that reduction of nitrobenzene to aniline occurs with utilization of both the CO and H₂ com-

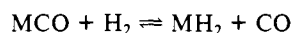
Table II

initial CO/H ₂ ratio	selectivity ratio substrate		
	nitrobenzene	<i>m</i> -dinitrobenzene	2,4-dinitrotoluene
0.33	1.03	1.01	0.95
1.0	0.92	0.95	0.98
3.0	1.07	0.99	0.97

ponents. At lower temperatures, with each catalyst system, there is a preference for utilization of the CO components but as the temperature of the reduction is increased so is the relative consumption of hydrogen. With Ir₄(CO)₁₂, even at 187 °C, there remains a preference for CO consumption, but with Rh₆(CO)₁₆ at 137 °C, the ratio of utilization of CO and H₂ is practically unity. The data are listed in Table I; the utilization of the CO and H₂ are indicated by the "selectivity ratio", defined as the ratio of CO/H₂ in the initial synthesis gas divided by the CO/H₂ ratio of the gases consumed in the reduction. A selectivity ratio of less than unity indicates a preference for utilization of CO while that of unity indicates utilization of CO and H₂ at the same ratio as their initial partial pressures.

With Rh₆(CO)₁₆ as the catalyst, and operating the reduction at 137 °C, we find that the selectivity ratio remains unity within experimental error for a variety of substrates such as nitrobenzene, *m*-dinitrobenzene, and 2,4-dinitrotoluene when equal pressures of CO and H₂ are used initially. Furthermore, with these substrates the selectivity ratio remains unity when the initial CO/H₂ ratio is changed to 3:1 and to 1:3. The data are presented in Table II. Thus, at 137 °C, Rh₆(CO)₁₆ is able to effect consumption of CO and H₂ at rates proportional to the partial pressures of these gases in the initial synthesis gas. The experiments were conducted in a batch reactor with a 1000:1 ratio of nitro group to catalyst; the products were >97% pure amino compound.

The above phenomena can be rationalized if we assume that there is established a rapid equilibrium between the species MCO (3) and MH₂ (4) under reaction conditions, as indicated in Scheme I, with an equilibrium under *K* (eq 3).



$$K = \frac{[\text{MH}_2][\text{CO}]}{[\text{MCO}][\text{H}_2]}$$

Therefore

$$\frac{[\text{MCO}]}{[\text{MH}_2]} = \frac{[\text{CO}]}{K[\text{H}_2]} \quad \dots \quad (3)$$

Since *k*_{CO} and *k*_{H₂} are the specific rate constants for the reactions of MCO and MH₂, respectively, then

$$\frac{\text{rate of utilization of CO}}{\text{rate of utilization of H}_2} = \frac{k_{\text{CO}}[\text{MCO}][\text{base}]}{k_{\text{H}_2}[\text{MH}_2][\text{base}]} = \dots \quad (4)$$

$$= \frac{k_{\text{CO}}[\text{CO}]}{Kk_{\text{H}_2}[\text{H}_2]} \quad (5)$$

K, *k*_{CO}, and *k*_{H₂} are each temperature dependent, and we find experimentally that the ratio of the rate of utilization of CO and H₂ is unity when [CO]/[H₂] = 1 (Table I). Therefore, at 137 °C, (*k*_{CO}/*k*_{H₂})/*K* = 1; substitution then in eq 5 gives eq 6.

$$\frac{\text{rate of utilization of CO}}{\text{rate of utilization of H}_2} = \frac{[\text{CO}]}{[\text{H}_2]} \quad \dots \quad (6)$$

It is concluded from eq 6 that any composition of synthesis gas could be used for these reductions and that the reduction will proceed, at 137 °C, such that the H₂ and CO will be consumed at a constant ratio given by their initial relative concentrations. The data given in Table II, in which reactions of CO/H₂ vary from 3:1 to 1:3, support this conclusion.⁴

(3) Reaction conditions: 0.05 mmol of catalyst, 42 mL of tetrahydrofuran, and 40 mL of 25% aqueous trimethylamine were added to a 0.31-L pressure reactor. The pressure reactor was pressurized with 390 mmol of carbon monoxide and hydrogen in a molar ratio of 1:1, 3:1, or 1:3, giving a total pressure of ca. 600 psi. Gas composition was determined prior to heating by gas chromatography. The reactor was heated and equilibrated to the indicated temperature before the addition of the nitroarene. Reaction times were 0.5 h for nitrobenzene and 3 h for 2,4-dinitrotoluene and *m*-dinitrobenzene. Gas composition was determined, after cooling to room temperature.

Acknowledgment. We thank the Robert E. Welch Foundation, the National Science Foundation, and the Department of Energy for financial assistance.

(4) Consistent with this analysis is the fact that of the several variables employed the selectivity ratio appears to be sensitive only to temperature. For example, in duplicate runs, with $\text{CO}/\text{H}_2 = 1$, but with twice the base concentration as given in ref 3, the selectivity ratios were 1.05 and 1.06 for the reduction of *m*-dinitrobenzene with $\text{Rh}_6(\text{CO})_{16}$ at 137 °C.

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Intramolecular Proton Exchange in Aqueous Histamine. An NMR Method for Resolving the Ammonium and Imidazole Proton-Exchange Rates

Sir:

We report an NMR method for the separate measurement of the rates of proton exchange in aqueous polyfunctional amines. The method has been applied to the aqueous histammonium ion which has two functional groups that are both magnetically and chemically distinguishable, namely, the alkyammonium protons of the histamine side chain and the imino protons of the imidazole ring. Histamine is of particular interest because of the possibility of intramolecular proton transfer which could act as a simple model for enzymatic catalysis.^{1,2} Extensive occurrence of the imidazole group at the active sites of many enzymes is well established,^{3,4} and it has been repeatedly emphasized that general acid-base catalysis is important in enzyme mechanisms,^{1,2,5-7} especially when one of the active functional groups is the imidazole ring.⁴

Methods available for the investigation of rapid reactions in solution have been described in detail.⁵ In relaxation methods such as temperature or pressure jump, the coupling between the perturbation and the extent of reaction depends on the magnitude of ΔH° or ΔV° , respectively. When a proton is transferred from one nitrogen atom to another, however, ΔH° and ΔV° will be very small (or even zero if the reaction is perfectly symmetrical), and hence the relaxation methods are insensitive to the rate for such a reaction. Also, because these reactions are fast, it is not possible to determine the separate proton-transfer rates directly by observing the two N-H resonances in the NMR spectrum since these resonances are exchange averaged with the water resonance, except at low pH.

The present method is based on measurements of the longitudinal relaxation time in the rotating frame ($T_{1\rho}$)^{9,10} of the dominant water resonance wherein the exchange broadening (Δ) is given by eq 1, in which T_1 is the spin-lattice relaxation time. If direct

$$\Delta = (1/T_{1\rho}) - (1/T_1) \quad (1)$$

(1) Bruice, T. C.; Benkovic, S. J. "Bio-Organic Mechanisms"; W. A. Benjamin: New York, 1966; Vol. 1, p 119.

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(9) $T_{1\rho}$ was determined by the adiabatic half-passage technique¹⁰⁻¹² at 25.0 °C at 100 MHz. T_1 was measured by the saturation recovery method.

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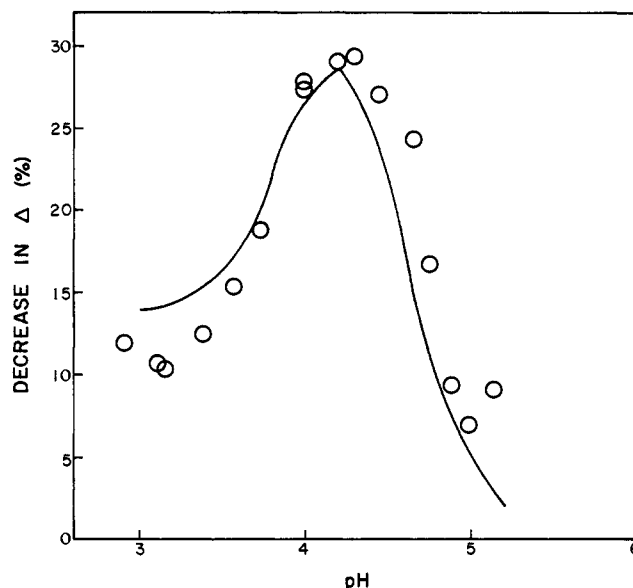


Figure 1. Reduction in exchange broadening vs. pH for 0.0596 M histamine. Δ is measured with $\omega_1 = 200$ and 2513 s^{-1} . The solid curve was computed from the rate law, eq 3.

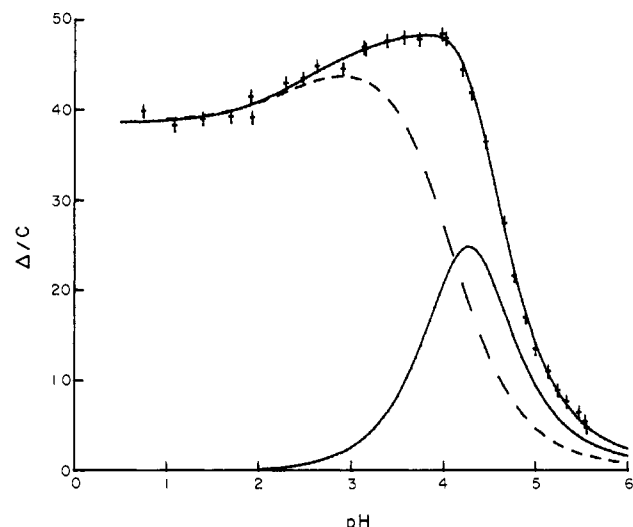


Figure 2. Δ/C vs. pH for 0.0596 M histamine. The upper solid curve is calculated from the rate law and eq 2 with $\omega_1 = 200 \text{ s}^{-1}$; the dashed line is the calculated imidazole contribution; the lower solid curve is the calculated ammonium contribution.

exchange between the imidazole NH protons (IMH^+) and amino protons (NH_3^+) is slow, then

$$\Delta = \frac{P_{\text{IMH}^+} \delta_{\text{IMH}^+}^2 \tau_{\text{IMH}^+}}{1 + \tau_{\text{IMH}^+}^2 (\delta_{\text{IMH}^+}^2 + \omega_1^2)} + \frac{P_{\text{NH}_3^+} \delta_{\text{NH}_3^+}^2 \tau_{\text{NH}_3^+}}{1 + \tau_{\text{NH}_3^+}^2 (\delta_{\text{NH}_3^+}^2 + \omega_1^2)} \quad (2)$$

where p represents the proton fractions, δ values are the water to NH chemical shifts in rad s^{-1} , τ represents the mean lifetimes, and ω_1 is the RF field strength. The two terms in eq 1 can be examined separately by varying ω_1 and utilizing the fact that δ_{IMH^+} and $\delta_{\text{NH}_3^+}$ are quite different. In 6 M HCl, where proton exchange is slow, two NH resonances are observed at 3.1 (1948 rad s^{-1}) and 8.3 ppm (5215 rad s^{-1}) relative to water, and these are assigned to the ammonium and imidazolium protons, respectively.^{13,14}

(13) Meyer, L. H.; Saika, A.; Gutowski, H. S. *J. Am. Chem. Soc.* **1953**, *75*, 4567.

(14) Δ/C is the exchange broadening divided by the molar histamine concentration; $P_{\text{IMH}^+} = C/111$, $P_{\text{NH}_3^+} = C/167$.