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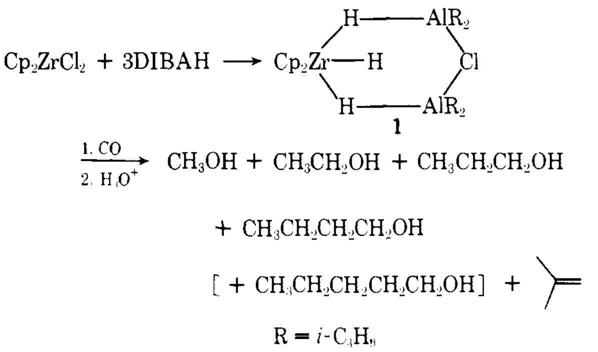
Reduction of Carbon Monoxide to Linear Alcohols by Aluminum Hydrides and Zirconium Complex Catalysts at Room Temperature

Sir:

Current interest in homogeneous analogues of the Fischer–Tropsch process derives from the desire to selectively convert coal, via CO, to hydrocarbon products which can serve as fuels or as feedstocks for other petrochemical processes.[1] Thus far stoichiometric conversion of CO to CH_3OH has been accomplished[2] and reports associated with the catalytic conversion of CO to CH_4[3] or to ethylene glycol[4] have appeared. The Fischer–Tropsch process is especially remarkable, though, in that multicarbon-containing fragments are produced. However, only one report of reductive polymerization of CO, accomplished homogeneously, has yet appeared.[5] All known Fischer–Tropsch-type processes, either heterogeneously or homogeneously accomplished, require elevated temperatures. We have recently found that DIBAH (i-Bu_2AlH) in the presence of Cp_2ZrCl_2 as a catalyst will reduce CO *at room temperature* and 1-4 atm to give, on hydrolysis, a mixture of linear aliphatic alcohols. We wish to report now the results of these studies.

Dissolving Cp_2ZrCl_2 in benzene in the presence of 3 equiv of DIBAH leads to the rapid formation of **1** (and 1 equiv of i-Bu_2AlCl).[6] This complex absorbs approximately 2 equiv of CO (based on Zr) over a period of 24 h (at room temperature) to give a golden yellow solution and to precipitate the Cp_2ZrCl_2 starting material. Addition of 3 equiv more of DIBAH leads to absorption of 2 equiv more of CO; this sequential procedure has been repeated over 10 times with no change in the stoichiometry of CO uptake relative to Zr. ^1H and ^{13}C NMR analysis of the golden yellow oily material obtained on evaporation of volatiles and removal of Cp_2ZrCl_2 indicates that it is a complex mixture of aluminum alkyls (no resonance attributable to a simple aluminum alkoxide is observable in the ^{13}C NMR spectrum).[7] IR (film) analysis indicates the absence of carbonyl absorptions but reveals strong bands attributable to C-O and Al-O-Al units.[8] NMR and VPC analysis of the volatile fraction obtained in this separation indicates that a substantial amount of isobutylene is produced concomitant with CO uptake.[9] It therefore appears that DIBAH can serve as the source of more than one hydride unit in such a CO reduction procedure.[10]

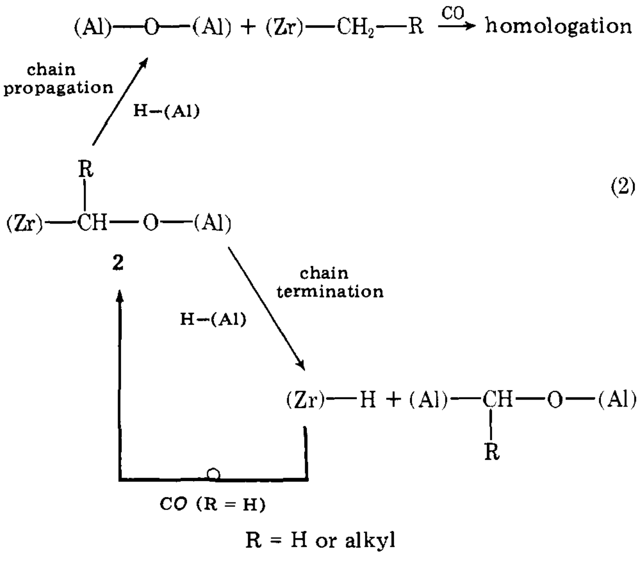
Treatment of the oily product of CO absorption with H_2O/H_2SO_4 yields, as shown by NMR and VPC analyses, methanol, ethanol, propanol, and 1-butanol, with an indication of 1-pentanol. For the mixture of Cp_2ZrCl_2 + 3DIBAH + CO (1 atm), methanol, ethanol, 1-propanol, and 1-butanol were obtained in the molar ratio 1.00:0.12:0.15:0.03 (or, based on CO incorporation, 1.00:0.24:0.45:0.12). That these linear alcohols are derived from CO was easily established using ^{13}CO. Here NMR analysis for CH_3OH showed it to be essentially all $^{13}CH_3OH$.[11] GC/mass spectral analysis confirms this determination for methanol and establishes that the homologous alcohols are formed by incorporating CO into *each carbon unit* of the alkyl chain (reaction 1).



(1)

It is important to note that, whereas **1** reacts readily with CO at 1 atm, excess DIBAH retards the uptake of CO (at 1 atm) although, as mentioned, the process done batchwise enables many turnovers based on Zr to be accomplished. In contrast, at 50 psi CO, reduction of CO in the presence of even 30 equiv of DIBAH occurs. Here, methanol, ethanol, 1-propanol, and 1-butanol in the molar ratio of 1.00:0.09:0.05:0.03 were produced (or, based on CO incorporation, 1.00:0.18: 0.15:0.12). Intriguingly, distributions of alcohols obtained in these sequences are reminiscent of those observed for linear hydrocarbon products of known Fischer–Tropsch catalytic sequences.[12]

Our results suggest a mechanism in which DIBAH dissociates from **1** to provide a vacant coordination site on Zr. Initial reduction of coordinated CO could occur either by H migration[2] from Zr or by (intramolecular) attack by "external" Al-H.[13] Polymerization of CO may occur via units such as **2**[14] in which chain propagation or termination occurs as shown in reaction 2. Transmetalation of alkyl groups from Zr to Al in exchange for -H has been established[6] and the reduction in this "carbenoid" complex of C-O-Al to H-C by DIBAH is not unreasonable. These results, too, support the contention[3,5] that multinuclear systems may be more useful for reductively *polymerizing* CO than are mononuclear ones. In this regard mixed-metal systems, especially those involving CO coordinators in combination with an oxygen-loving Lewis acid, may prove to be especially effective. Control of product distribution as well as mechanistic details of the fascinating transformation described herein are now under study.



(2)

Acknowledgment. The authors acknowledge generous support provided for this work by the NSF (CHE 76-02130).

References and Notes

(1) For a recent review of this process, see G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **15,** 136 (1976).

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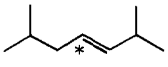
(7) ^{13}C NMR for $(i\text{-}C_4H_9)_2Al{-}O{-}CH(CH_3)_2$, δ 67 (prepared from $(i\text{-}C_4H_9)_2AlH$ and acetone).

(8) T. J. Hurley, M. A. Robinson, J. A. Scruggs, and S. I. Trotz, *Inorg. Chem.*, **6,** 1310 (1967).

(9) Olefins **3** and **4** and 2-methyl-4-butanol are also obtained as by-products presumably by alkylation of CO, reduction, and, for **3** and **4,** elimination.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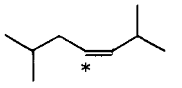
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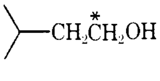

The assignment of structures for **3** and **4** is based on ^1H and ^{13}C NMR and mass spectral analysis. Using labeled ^{13}CO, it is observed that carbons marked (*) are specifically enhanced in ^{13}C. A small amount of 2-methyl-1-propanol is also observed. This alcohol is likely formed from adventitious oxygen in the workup procedure and contains no ^{13}C (above natural abundance) when ^{13}CO is used. Approximate amounts of **3** and **4** (combined) and 2-methyl-4-butanol, relative to CH_3OH (for Zr:Al::1:3), are 0.5 and 0.07, respectively.

(10) β-Hydride loss from DIBAH at 110 °C is well known. Under these much milder conditions it is possible that a Zr species acts to *abstract* this hydride. Such β-hydride abstraction from main group alkyls is well precedented (for example, see J. M. Jerkunica and T. G. Traylor, *J. Am. Chem. Soc.*, **93,** 6278 (1971)).

(11) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Am. Chem. Soc.*, **92,** 1 (1970).

(12) H. Pichler, H. Schulz, and M. Elstner, *Brennst. Chem.*, **48,** 78 (1967); M. A. Vannice, *J. Catal.* **37,** 449 (1975).

(13) This sequence parallels results obtained for the reduction of transition metal carbonyls by $NaBH_4$ (C. P. Casey and S. M. Neumann, *J. Am. Chem. Soc.*, **98,** 5395 (1976)).

(14) A scheme for reductive polymerization of CO in the Fischer–Tropsch process has been proposed.[1]

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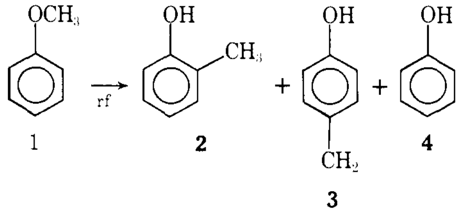
Kinetics of Anisole Plasmolysis

Sir:

Organic reactions induced by a glow discharge plasma have been used for purposes as diverse and exotic as modelling prebiotic synthesis, investigation of gas phase, organic ion chemistry, the preparation of thin polymer films, surface modification of solids, and organic synthesis.[1] Interpretation and application of the results of all of these studies are, however, hampered by the absence of a fundamental understanding of the dynamics and mechanisms in reactive, organic plasmas. We have sought to rectify this situation and have undertaken studies of the cool plasmas generated in a radio-frequency discharge. We demonstrate here the feasibility of applying kinetic methods and relate the observations to a theory in which the number and energy of the electrons in the plasma control the rate of reaction and, therefore, to a certain extent also the product ratios.

The apparatus is very similar to that previously described[2] except that dual reactant reservoirs were used. This allowed two compounds to be simultaneously flowed through the reactor with independently controlled flow rate. A bulb-to-bulb distillation at pressures from 0.02 to 0.2 Torr flows material through the discharge zone. A 13.6-MHz radio-frequency generator is inductively coupled to the system via a copper coil wound around the outside of the glass reaction tube and when power is applied a plasma, an ionized gas, is produced. After the material exits from the plasma it is collected in a liquid nitrogen trap and eventually analyzed by gas chromatography. The applied power (P) was measured and in every case the circuit was balanced so that the reflected power was negligible. Flow rate (r) was calculated from the amount of material lost from the reactant reservoir and the elapsed time during plasmolysis.

The plasmolysis of anisole (**1**) was chosen for study. Suhr and Weiss[3,4] had previously investigated this reaction and found the major products to be *o*-cresol (**2**), *p*-cresol (**3**), and phenol (**4**). *m*-Cresol, benzene, toluene, methylcresols, and methylcyclopentadiene were present in 0–3% yield. A number of aryl ethers and alkylanilines were shown to react similarly. The isomerization to form *o,p*-cresol is a simple, yet unique, reaction and has been proposed to involve an intermolecular, ionic mechanism. Therefore, this was an especially interesting reaction for further study.



Anisole plasmolysis gave the products previously reported and some polymer. The extent of conversion of anisole (the rate) and the product ratio[5] depends on the applied power (P) and the flow rate (r). Qualitatively, low P and/or high r give low conversion and favor the formation of the cresols over phenol. This kind of observation has been previously reported for the reaction of 2-butene and arguments were put forward there to support the idea that the number and energy of the electrons in the plasma controlled both the rate and product ratio in that reaction.[2]

Quantitative interpretation of the anisole data depends upon the accepted mechanism for sustaining a discharge.[6] In this mechanism the rf field accelerates the few free electrons in the gas and by electron impact these cause further ionization until a steady state is reached. The resulting plasma is a nonequilibrium mixture in which the electrons have a relatively high temperature (kinetic energy), but the neutrals are near ambient. It may be speculated from other studies that the degree of ionization is low ($\sim 5 \times 10^{11}$ electrons/cm^3) and that the electron energies should have an approximately Maxwellian distribution with a mean energy of a few electron volts. It is accepted that organic molecules which pass through the discharge region are primarily activated by electron impact. The rate of reaction and the type of reaction products will, therefore, depend on the number and energy of the electrons, the electron energy function, $f(\epsilon)$.[6]

Assuming that the rate-determining step is impact of a suitably energetic electron on anisole, the following integrated rate equation can be written

$$-\ln (p_1/p_1{}^0) = k\tau f(\epsilon)$$

where τ is the residence time in the plasma, $p_1{}^0$ is the pressure of **1** at entrance into the plasma and p_1 is the anisole pressure at exit from the plasma zone. Thus $p_1/p_1{}^0$ can be equated to the fraction of **1** recovered ($[\mathbf{1}]/[\mathbf{1}]_0$). Note that there are two parts to the right-hand side of this equation, an anisole plus electron rate and $f(\epsilon)$ which expresses the dependence of rate on the number of electrons and the electron energy distribution. This part can be used to describe the effect of varying P, r, or p on the rate.[7] The precise form of the dependence of k on these experimental variables is not known and may be complex. It is, however, clear that k should be some function of P/p.[6] We