The influence of ion-pair equilibria can be neglected since the hyperfine data are not substantially affected when replacing the potassium/crown ether counterion by benzyltrimethylammonium (Table II). Moreover, the results obtained in 8CB demonstrate that the isotropic hyperfine couplings are not significantly altered when passing from the isotropic to the smectic phase. Consequently, the phase transition is not accompanied by a substantial change in the solvation or the ion-pair structure. It should be noted that the isotropic coupling constants of **2** in liquid crystalline solvents are in agreement with those obtained in dimethylformamide.[15] A similar invariance is found for the large coupling of **1** (−2.73 ± 0.01 MHz, ethanol or toluene), whereas the small coupling is strongly solvent and temperature dependent (−1.53 MHz, ethanol, 210 K; −1.33 MHz, toluene, 210 K; −0.89 MHz, 8CB, 315 K). This probably accounts for the anomalous temperature behavior of the shifts of **1** in "phase IV" (Table I).

Since there is considerable interest in studying quadrupole splittings by means of ENDOR in liquid crystals, it is noteworthy that we succeeded in observing deuterium quadrupole splittings in the ENDOR spectrum of **3**. The splitting amounts to about 160 kHz for the para positions (8CB, 294 K), whereas splittings for the ortho or meta positions could not be resolved.

^2H ENDOR quadrupole splittings are strongly dependent on the orientation of the C–D bond, being largest for an orientation parallel to the magnetic field.[3] Therefore, a trans configuration of **3** can be assumed, and the long axes of the molecules are preferentially oriented parallel to the long axes of the solvent molecules. Further ENDOR studies of radical ions in liquid crystals are in progress.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Normalverfahren) and by the Fonds der Chemischen Industrie which is gratefully acknowledged.

---

(15) Dehl, R.; Fraenkel, G. K. *J. Chem. Phys.* **1963**, *39*, 1793.

B. Kirste, H. Kurreck*
Institut für Organische Chemie, Freie Universität Berlin
1000 Berlin 33, West Germany

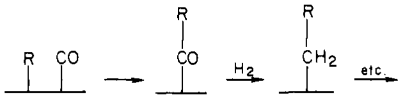
Received May 12, 1980

Reactions of Diazomethane on Transition-Metal Surfaces and Their Relationship to the Mechanism of the Fischer-Tropsch Reaction

Sir:

We report results of experiments which are consistent with the original proposal of Fischer and Tropsch made in 1926 that the formation of hydrocarbons produced upon reaction of CO and H_2 on certain transition-metal surfaces (the Fischer-Tropsch reaction) proceeds via "polymerization of methylene groups" on the metal surface.[1] The methylene groups were suggested to arise by reduction with H_2 of carbon atoms formed, following decomposition of CO on the metal.

An alterative mechanism, which subsequently has received widespread acceptance, was one in which the C–C bonds of the product were initially derived from insertion of adsorbed CO molecules into metal-alkyl groups on the surface.[2] Reduction of the acyl group to an alkyl group and repetition of the insertion of CO were proposed to lead to chain growth (eq 1). This proposal derived credibility from the well-established phenomenon in homogeneous organometallic systems of the insertion of CO ligands into metal-alkyl bonds, leading to metal-acyl derivatives.



(1)

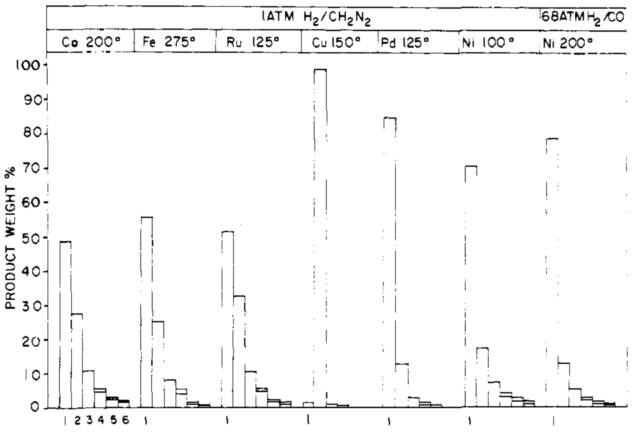


Figure 1. Hydrocarbon product weight distributions over various supported transition metals: saturated and olefinic products are indicated together; the distribution of linear to branched products is indicated by the intermediate line, the linear materials given by the lower section.

However, recent studies have confirmed the dissociative chemisorption of CO on single-crystal metal surfaces and strongly implicate the role of this step in the formation of hydrocarbons when H_2 is present.[3]

The nature of the reaction of CO and H_2 over various transition metals varies markedly with the particular metal. Over metals such as Fe, Co, and Ru (Fischer-Tropsch catalysts), there is produced a mixture of hydrocarbons, the exact nature of the product further depending on the particular reaction conditions employed (temperature, pressure, CO/H_2 ratio, flow rate, etc.), but the mixture characteristically consists of linear alkanes and monoolefins with lesser amounts of nonlinear isomers. The components may range from methane to high molecular weight material resembling linear polyethylene. With Ni and Pd, methane is the principal product formed while with Cu there is no reaction.

To answer the question as to how methylene groups would behave on a metal surface, we have examined the products of the reaction of diazomethane (CH_2N_2) with and without H_2 over various transition metals with the expectation that dissociative chemisorption of CH_2N_2 to absorbed methylene groups and N_2 would occur. The gas-phase thermal decomposition of diazomethane at 290–400 °C has previously ben studied and is found to produce mainly CH_4, C_2H_6, C_2H_4, C_2H_2, and HCN; when excess H_2 is present, the products are primarily CH_4 and C_2H_6.[4] The reaction is interpreted in terms of intermediate formation of CH_2 fragments, but significant amounts of polymerization to higher hydrocarbons were not observed.[5]

We find that CH_2N_2,[6] diluted with an inert gas (He or N_2) is rapidly and quantitatively decomposed upon passage over Ni, Pd, Fe, Co, Ru, and Cu surfaces[7] at 1 atmosphere of pressure and in the temperature range 25–200 °C, and in each case ethylene

---

(1) Fischer, F.; Tropsch, H. *Brennst.*-Chem. **1926**, *7*, 97–116.

(2) (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103; (b) Henrici-Olivé, G; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136–141. (c) *Ibid.* and references therein.

(3) For recent reviews, see, e.g.: Ponec, V.; van Barneveld, W. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 268–271. Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *80*, 479–490.

(4) Dunning, W. J.; McCain, C. C. *J. Chem. Soc. B* **1966**, 68–72.

(5) The liquid-phase decomposition of ethereal solutions of CH_2N_2 over extended periods (8–24 h) on surfaces such as procelain or on metals such as Cu or Au leads to the formation of polymethylene; see: Nasini, A. G.; Trosserelli, L.; Saini, G. *Makromol. Chem.* **1961**, *44–46*, 550–569.

(6) Typically, a solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in anisole is pumped into a stirring solution of aqueous KOH in 2-(2-ethoxyethoxy)ethanol and the generated diazomethane is swept from the reaction flask with an inert gas through a KOH drying tube. The diluted diazomethane can then be mixed with other gases before entering a heated glass tubular reactor containing the catalyst.

(7) The Fe, Co, and Ni catalysts were obtained from the Harshaw Chemical Co. The Pd, Ru, and Cu catalysts were prepared by deposition of the chloride or nitrate salts from aqueous solution on a support (Cab-O-Sil or kieselguhr). All catalysts were reduced at 400 °C in a stream of H_2.

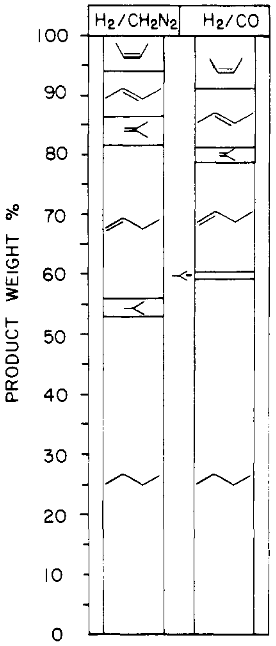
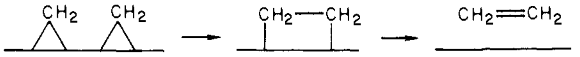


Figure 2. Comparison of four-carbon isomer distributions obtained with H_2/CH_2N_2 and H_2/CO over a 39% Co/kieselguhr catalyst at 210 °C and 1-atmosphere pressure.

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]



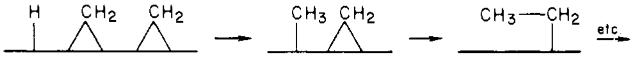
(2)

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) 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 CH_2N_2/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 CH_2N_2/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



(3)

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 CH_2N_2/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.

---

(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 prepration 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.

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

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

Robert C. Brady III, R. Pettit*
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

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 agent[2] (eq 2).

$$S + H_2 \rightarrow SH_2 \qquad (1)$$

$$S + CO + H_2O \rightarrow SH_2 + CO_2 \qquad (2)$$

---

(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.