

THE CHEMISTRY AND CATALYTIC PROPERTIES OF COBALT AND IRON CARBONYLS ¹

By

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Summary

A STUDY of the metal carbonyls and their catalytic action has revealed the existence of a new chemistry. Perhaps the most important result of this work has been the discovery of the catalytic action of the hydrocarbons of cobalt and iron, probably a consequence of the unusual structure of these compounds. The hydrogen in cobalt hydrocarbonyl is not attached to the metal or to an oxygen atom, as previously assumed. Although the hydrogen is acidic, the nature of the metal-hydrogen bond in the hydrocarbons is not explainable in terms of any known bonds; the hydrogen is some distance from the metal and is associated with the carbon monoxide groups. This is remarkably similar to the state of events on a metal surface treated with carbon monoxide and hydrogen. Here, despite the fact that the hydrogen atom can easily get into the interstitial position, it prefers to remain "outside" the surface, between the carbon monoxide group, where it carries a positive charge (is acidic). The hydrogen in the metal hydrocarbons and the hydrogen on a metal surface covered with synthesis gas are both easily detached and, most important, highly reactive.

The catalytic reactivity of the hydrocarbons is remarkable. Pure cobalt hydrocarbonyl, for example, will hydrogenate certain olefins to paraffins, ketones to alcohols, and aromatic alcohols to hydrocarbons, all at room temperature or below. A catalytic amount of iron or cobalt hydrocarbonyl will rapidly isomerize terminal olefins to internal olefins. Directly pertinent to the Fischer-Tropsch reaction is the fact that olefins react stoichiometrically at room temperature with cobalt hydrocarbonyl to form the next higher aldehyde. There are few if any ways of lengthening a carbon chain in synthetic organic chemistry that proceed with such ease. This lengthens the carbon chain by one carbon, and a very similar mechanism of chain lengthening must occur in the Fischer-Tropsch reaction. Evidence from a study of the kinetics of the hydroformylation (oxo) reaction makes it likely that the olefin first forms a complex with dicobalt octacarbonyl or cobalt hydrocarbonyl.

A study of the chemical behavior of dicobalt octacarbonyl towards unsaturated hydrocarbons has led to the discovery of a new type of organometallic complex derived from the carbonyl and acetylene. This binuclear complex is of considerable interest, since it resembles a type of surface intermediate postulated for the Fischer-Tropsch reaction. Chain lengthening of the unsaturated molecules takes place when this acetylene complex is treated with alcohol and acid.

The reaction of iron pentacarbonyl in alkaline aqueous solution, and especially the reducing properties of these solutions, has been studied. Partic-

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ularly interesting is the finding that reduction in this system is achieved by the transfer of hydrogen from adjacent metal atoms, a mechanism analogous to hydrogenation on metal surfaces.

The determination and interpretation of the infrared spectra of various metal carbonyl cations and anions have established the fact that the metal-carbon and carbon-oxygen bond strengths in the metal carbonyls vary with the amount of formal charge on the metal atom.

The metal carbonyls have been found to be excellent catalysts at elevated temperatures and pressures for a number of reactions. None of these homogeneously catalyzed reactions is poisoned by sulfur compounds. They include the hydrogenation of aldehydes and ketones to alcohols, the homologation of alcohols (that is, the conversion of methanol to ethanol), the reduction of aromatic alcohols and ketones to hydrocarbons, the hydrogenation of thiophenes, and the selective hydrogenation of polynuclear aromatic compounds. In the cobalt carbonyl catalyzed reaction of benzyl alcohols with synthesis gas, electron-releasing groups on the ring favor chain lengthening; electron-attracting groups favor hydrogenation to the corresponding toluenes.

INTRODUCTION

There are, at present, two processes for the synthesis of liquid fuels: The Fischer-Tropsch process, which involves the catalytic conversion of carbon monoxide and hydrogen to liquid fuels, and the coal hydrogenation process, which is concerned with the catalytic hydrogenation of coal at high pressure. Both rely on coal as the primary source of carbon and hydrogen, and both are catalytic processes involving a heterogeneous hydrogenation catalyst. The technology of the coal hydrogenation process is more familiar, for the catalytic hydrogenation and hydrogenolysis of organic compounds are well-known reactions; however, due in part to the inherent difficulty in studying heterogeneously catalyzed reactions, little is known of the intimate mechanism of catalytic hydrogenation. The pathway to liquid fuels by means of the Fischer-Tropsch process involves the catalytic addition of hydrogen by a carbon monoxide-poisoned surface, a somewhat puzzling phenomenon. Coal hydrogenation starts with the complex coal molecule and breaks it down to simpler molecules by thermal and catalytic processes; the Fischer-Tropsch process involves the formation of complex molecules of the same type by the ordered condensation of carbon monoxide and hydrogen on the surface of a transition metal.

Both processes have been studied at the Bureau of Mines, and summaries of these investigations are available. In the direct approach to both reactions, much has been learned about their nature. The studies discussed here were an outgrowth of work on the Fischer-Tropsch reaction, but the attack on the problem was made from an entirely different angle. The basis necessary for this new approach rests on the following observations:

1. In 1947, Pichler pointed out that the optimum conditions for the Fischer-Tropsch process prevail at pressures just below those at which (at the corresponding temperatures) the tendency towards the formation of volatile carbonyls becomes so great that the catalyst deteriorates. Conditions for the Fischer-Tropsch reaction must be such that volatile carbonyls form somewhat more slowly than do the supposed intermediate carbon monoxide compounds with hydrogen. In discussions of the reaction, Pichler stressed the fact that all Fischer-Tropsch catalysts yield detectable amounts of metal carbonyls at optimum reaction temperatures and pressures.

2. In 1929, Smith, Hawk, and Golden, who were studying the Fischer-Tropsch reaction at the Bureau of Mines, added ethylene to the carbon monoxide-hydrogen mixture before passing it over a cobalt catalyst and found that the yield of oxygenated compounds was increased. Roelen, one of Franz Fischer's former students, used the same approach in his study of the Fischer-Tropsch synthesis and discovered an entirely new reaction—the oxo or hydroformylation reaction. Roelen postulated that a cobalt carbonyl was the catalyst in the formation of propionaldehyde from ethylene. Since the metal carbonyls are soluble in organic liquids and oils, this discovery led to the possibility of studying simpler, homogeneously catalyzed reactions of carbon monoxide and hydrogen.

3. Very early work at the Bureau revealed the fact that carbonyls of cobalt homogeneously catalyzed the oxo reaction, in which molecular hydrogen is split. Previously, the catalytic utilization of hydrogen had always been associated with activation by metallic surfaces. Here, then, was a soluble isolatable analog of a metal surface capable of catalyzing the addition of carbon monoxide and hydrogen to unsaturated bonds in organic molecules. The application to the general field of catalysis and to the Fischer-Tropsch reaction was now at hand.

4. The type of bonding in metal carbonyls has been a perennial thorn in the side of a constantly advancing valence theory. The transition metal-carbon bond is rare, and the drive to elucidate the nature of this bond was spurred by the discovery that metal carbonyls may function as catalysts. Hydrocarbons of the transition metals were known at the start of these investigations, and the role of these compounds, in which the nature of the bonding of the hydrogen was only faintly surmised, now became of the utmost importance.

This background enables us to present the objectives of this work. It is important to present these aims at this time, for they have continually furnished the directions of our lines of thought. Although the objectives and plans have emerged from studies of the Fischer-Tropsch reaction, the most general purpose has been to conduct fundamental studies on the mechanism of catalytic action. The homogeneous activation of hydrogen by soluble catalysts allows the results to be applied to both the hydrogenation of coal and the Fischer-Tropsch synthesis. The opportunity to study the mechanism of chain lengthening and the nature of surface intermediates in the Fischer-Tropsch reaction is both obvious and unique.

This report is divided into three parts, although the studies were carried out simultaneously.

With few exceptions, this report covers work performed through 1957.

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