JOURNAL OF CATALYSIS 23, 374-378 (1971)

Infrared Spectra of C_2H_4 Adsorption and CO Insertion Reactions on an Fe Surface

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Received April 16, 1971; accepted May 11, 1971

Infrared spectra indicate that ethylene and hydrogen coadsorb on iron to produce ethyl groups. Unless the iron surface is first pretreated with hydrogen, very little ethylene adsorbs. In direct analogy to insertion reactions of coordination complexes, the reaction of carbon monoxide with a surface alkyl has been shown to occur on an evaporated iron surface to produce an isopropoxide species. Using infrared spectroscopy the reaction was followed from known surface reactants to known surface products.

INTRODUCTION

While chemical reactions induced by surfaces have been the object of many investigations, the actual changes in structure of species while on the surface have generally been inferred by indirect evidence rather than being studied directly. Conventionally catalytic or surface reactions are divided into five steps; diffusion to the surface, adsorption, reaction on the surface, desorption, and diffusion away from the surface. In all but a few instances in investigations of catalytic reactions and even in molecular beam experiments, the state of the reactants in the gas phase is carefully defined and the state of the products precisely determined. From these initial and final states of the system, something about the surface processes is then inferred. We wished to make more direct observations on the surface and here apply infrared spectroscopy to that end. Our aim was to determine by infrared spectra the structure of a potential reactant while adsorbed on the surface, induce a reaction, and then spectroscopically determine the structure of the products on the surface.

When considering surface reactions analogies to the structure and reactions of coordination complexes have been suggested by a number of authors (*1–5*). However, there are very few data available which allow direct comparison of homogeneous coordination complex reactions to heterogeneous reactions. The reaction mechanisms and transition states for coordination complexes are firmly based on a large body of good structural data. In strong contrast, very few data directly interpretable in terms of structure exist for surface species. If surface reactions are to be treated with the same assurance as other inorganic reactions, structural data about surface species are necessary. By choosing to examine a reaction on a metal surface that also occurs as a homogeneous coordination complex reaction, not only is detailed information about the structure and reactivity of surface complexes obtained but data to define the relationship between homogeneous and heterogeneous processes is gained.

The CO insertion reaction, one example of which is shown in Eq. (1), was chosen for study. This reaction is reasonably well characterized (*6–8*) as a coordination complex reaction but is unknown as a surface reaction. We first tried to obtain the CO insertion reaction on a Mn surface but

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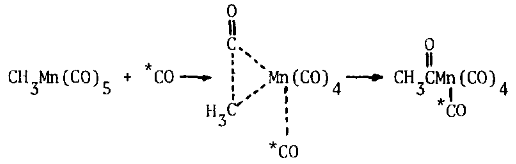


$$CH_3Mn(CO)_5 + {}^*CO \longrightarrow \underset{H_3C \quad {}^*CO}{\overset{O=C}{Mn}}(CO)_4 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\underset{{}^*CO}{Mn}(CO)_4 \qquad (1)$$

were unsuccessful. Our equipment does not lend itself to using the high CO pressures that are used in the homogeneous reactions and, therefore, we cannot say that the reaction does not occur on a Mn surface under the same conditions as the homogeneous reaction. However, an insertion reaction does occur on an Fe surface (*9*). Since the structures of hydrocarbons adsorbed on Fe have not been characterized it was first necessary to do this and these results are also reported here. The structure of adsorbed CO on Fe has received sufficient attention already (*10–13*) to characterize the surface complex.

Experimental

The wide spectral range experimental technique, which has been described in detail elsewhere (*10*), consists of evaporating Fe from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas phase deposit in a hydrocarbon oil film on the salt windows of an infrared cell. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species is obtained. Spectra are recorded before and after admission of the gas to the cell. Five minutes of pumping has been found sufficient to remove all spectra due to gas-phase molecules. For three- and four-carbon-atom molecules, 30 min of pumping may be required to remove molecules dissolved in the oil film. The spectra were obtained using Perkin–Elmer Models 21 and 337 spectrophotometers.

The iron was obtained from A. D. Mackay, Inc., as 10-mil high-purity wire and was used as supplied until just before the evaporation at which time the metal was fused to a tungsten filament. Carbon monoxide was obtained from Matheson Co., Inc., as C. P. grade and further purified by distilling three times from liquid air cooled traps and discarding the last portion of each distillation by pumping on the system. Hydrogen was also supplied by Matheson Co. Oxygen impurity was removed from the hydrogen by passing the gas over copper turnings at 420°C. The gas was then dried by passage through a trap cooled with liquid air. After drying, the hydrogen was passed through an activated charcoal trap cooled with liquid air.

Ethylene was obtained from Airco, Inc., and ethylene-d_4 from Isomet Corp. Both were distilled three times from liquid air cooled traps as described above.

This technique has the advantage that a wide infrared spectral region is available for study. It has the disadvantage that the metal surface is covered with oil. This oil is apparently only weakly adsorbed since many gases have been found to chemisorb readily on the metal. Essentially the oil is regarded as a solvent which has weak interactions with the systems of interest. Having a wide spectral range available aids greatly in attempts to determine structure.

Results

The results of measuring the volume of gas adsorbed on evaporated iron films, some of which had been pretreated with hydrogen and some of which were not so pretreated, are given in Table 1. These are measurements of the pressure decrease due to adsorption of successive 1 Torr increments of gas on iron evaporated onto

TABLE 1

Volume of Gas Adsorbed (Arbitrary Units) on Evaporated Fe

	C_2H_4	CO
Fe (no H_2 pretreatment)	93	660
Fe (H_2 preadsorbed)	252	

the walls of an evacuated Pyrex flask until the film would adsorb no more of the gas.

Admission of ethylene or ethylene-d_4 to the infrared cell with freshly evaporated-into-oil iron produced no detectable infrared bands for chemisorbed species. Likewise, addition of ethylene after hydrogen pretreatment produced no observable infrared bands for chemisorbed species. Adsorption of ethylene-d_4 after D_2 pretreatment results in the bands listed in Table 2. The relative intensities in the C–D stretching region resemble those for an ethyl-d_5 group, i.e., the highest frequency band is the most intense. Addition of more D_2 at this stage results in a 5 to 10% increase in intensity of the 2225 cm^{-1} band.

TABLE 2

INFRARED BANDS AFTER D_2 AND C_2D_4 ADSORPTION ON Fe

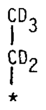
Band position	Assignment
2225 cm^{-1}	CD_3 asym str
2125 cm^{-1}	CD_2 asym str
2055 cm^{-1}	CD_3 and CD_2 sym str
1045 cm^{-1}	CD_2 deformation
950 cm^{-1}	CD_3 deformation

The reaction was induced by the following sequence; metal evaporation, addition of 50 Torr of H_2 for 10 min, pumping for 3 min, addition of 100 Torr of ethylene for 12 hr, pumping for 5 min, addition of 70 Torr of CO for 30 min, evacuation for 5 min, and heating at 100°C for 6 hr. The CO addition produced a strong infrared band at 1900 cm^{-1} which remained upon evacuation. After heating broad bands appeared at 1100 and 950 cm^{-1}.

Following a similar procedure but with deuterium replacing hydrogen gave broad bands at 1035 and 885 cm^{-1}. Doing the heating step with gas-phase CO in the cell did not change the results.

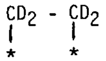
DISCUSSION

The data indicate that ethylene is chemisorbed on a hydrogen treated surface largely as ethyl groups, structure I.



$CD_3\text{–}CD_2\text{–}*$

(I)



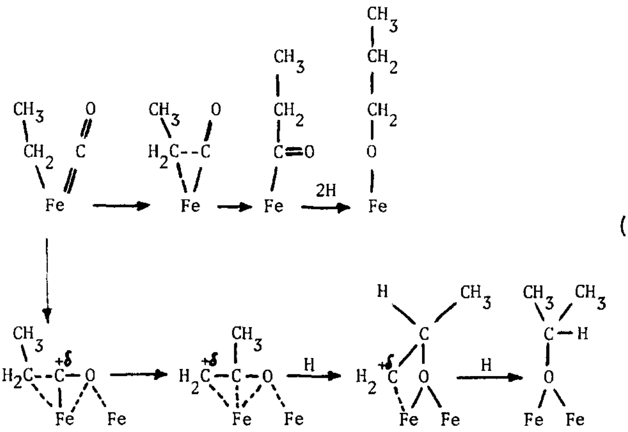
$*\text{–}CD_2\text{–}CD_2\text{–}*$

(II)

Evidence of structure I being present was provided by the fact that C–D stretching vibrations were observed for both CD_3 and CD_2 groups. Evidence of structure II was provided by the results of heating the sample with D_2 gas present. This caused the bands for CD_3 stretching vibrations to increase a little indicating that some of structure II was being hydrogenated to structure I. The volumetric and infrared data both indicate that relatively little ethylene adsorbs on an iron surface that is not pretreated with hydrogen. This suggests that there are relatively few surface sites with the proper geometry to produce stable species of structure II. The extent of CO adsorption after exposure of the surface to H_2 and C_2H_4 in both the volumetric and infrared data indicate that the ethylene does not cover a large portion of the surface. An effect of hydrogen pretreatment on ethylene adsorption on metal surfaces has been previously noted *(14)*. Because a π-adsorbed ethylene species has often been suggested this type of structure was considered. However, the absence of C–H or C–D stretching bands in a region attributable to unsaturated carbon atoms indicates that adsorption as either a π complex or a vinyl group occurs at most to only a small extent.

There is an indication that some interaction is occurring between the adsorbed ethyl groups and adsorbed CO even before the reaction is initiated by looking at the position of the carbonyl stretching frequency of adsorbed CO. A band is normally observed for this stretching frequency at 1950 cm^{-1} on freshly evaporated iron samples *(10)* and this band was also found to be unchanged due to the preadsorption of hydrogen.

The infrared band positions for the reaction product agree well with the most intense bands of an adsorbed isopropoxide species *(15)* and do not agree with those of an adsorbed *n*-propoxide species *(15)*. Since the reaction occurs with the gas phase evacuated, it is presumed to indeed be a reaction between adsorbed CO and the adsorbed ethyl group. By direct analogy to the insertion reactions of coordination complexes, one would expect an ethyl group migration to produce an acyl structure. However, the absence of an infrared band in the carbonyl stretching region indicates an acyl structure was not formed. Adsorption of aldehydes and ketones on an iron surface leads to alkoxide formation and so even if an acyl structure were formed, its hydrogenation on a surface previously exposed to hydrogen is not unexpected. In the simplest possible reaction a *n*-propoxide species would be produced as shown below but the infrared spectrum indicates an isopopoxide species and therefore a more complex process than that proceeding through step I. A suggested mechanism is presented below as going through step II.



The interaction of the carbonyl oxygen with Fe atoms could well lead to the production of a positive center at the carbonyl carbon and methyl migrations to positive centers are well known. As to whether the processes are concerted or stepwise, we are unable to say. The possibility of an *n*-propoxide structure being formed and then isomerizing to the isopropoxide structure was considered and rejected because in a separate experiment *n*-propanol was adsorbed on Fe to produce the *n*-proxide species which did not isomerize upon being heated at 100°C for 6 hr.

In summary it may be noted that a surface reaction has been successfully followed from a known surface reactant to a known surface product. The CO insertion reaction which occurs in homogeneous coordination complex reactions does occur on an Fe surface but the final product is different. The difference is attributable to the ready availability of hydrogen atoms in adjacent coordination positions to affect the reduction from an acyl to an alkoxide structure. These hydrogen atoms are not available in the homogeneous coordination complex reaction. This brings out that one of the differences between homogeneous and heterogeneous systems is that homogeneous systems are usually limited to reactions of the ligands on one metal atom, whereas in the heterogeneous case, species occupying ligand positions on nearby atoms may readily enter into reactions. Thus migration of the reactant molecules over the metal surface may facilitate the reaction.

ACKNOWLEDGMENT

This investigation was supported in part by a United States PHS Research Grant No. 00818-01 from the National Air Pollution Control Office.

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