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Studies of Silica-Supported Metal Chloride Catalysts for the Vapor-Phase Hydrochlorination of Acetylene

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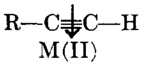
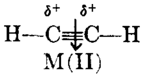
The first phase of a systematic examination of heterogeneously catalyzed vapor-phase reactions of acetylene with acids of the HQ type has involved infrared and reaction studies of silica-supported metal chloride catalysts. Examination of the infrared spectra of acetylene and propyne adsorbed on these catalysts has yielded information on the mode of adsorption. On all surfaces studied a species of the type



$$\mathrm{R{-}C}\underset{\mathrm{M(II)}}{\underset{\downarrow}{\equiv}}\mathrm{C{-}H}$$

is observed, where R is H and CH_3 and M(II) is Ca(II), Mn(II), Cu(II), and Zn(II). Shifts of propyne –C≡C– as well as propyne and acetylene ≡C–H vibrations to lower frequencies on adsorption in this configuration are related to the electron affinities of the metal ions. Studies of the catalytic activities of silica-supported Hg(II), Bi(III), Ni(II), Zn(II), Cd(II), Cu(II), Mn(II), and Ca(II) chlorides for the vapor-phase hydrochlorination of acetylene have supplemented literature information and provided some basis for interpretation of the infrared results. After a rapid decline from a higher initial activity, a nearly steady activity is attained yielding the order Hg(II) > Bi(III) > Ni(II) > Zn(II) > Cd(II) > Cu(II) > Mn(II) > Ca(II). It is possible to rationalize spectroscopic data obtained so far with the observed order of catalyst activity in terms of the adsorbed species



$$\mathrm{H{-}}\overset{\delta^+}{\mathrm{C}}\underset{\mathrm{M(II)}}{\underset{\downarrow}{\equiv}}\overset{\delta^+}{\mathrm{C}}\mathrm{{-}H}$$

INTRODUCTION

Heterogeneously catalyzed reactions of acetylene with HQ compounds

$$HC{\equiv}CH + HQ \xrightarrow{\text{Catalyst}} H_2C{=}CHQ$$

where Q^- may be halide, hydroxide, acetate, etc., are of practical and theoretical importance. Considerable information has accumulated to indicate that transition metal compounds are the best catalysts for reactions of this type. Some of these reactions and frequently employed catalysts are listed in Table 1. Empirical generalizations concerning the dependence of catalyst activity on catalyst composition have resulted from investigations of the thermodynamic and kinetic aspects of the reactions of acetylene with H_2O, HCl, and CH_3COOH.

Gorin and Gorn studied the vapor-phase catalytic hydration of acetylene over solid catalysts in an attempt to determine the effect of various cations (*1*) and anions (*2*) on the conversion of acetylene to acetaldehyde. Several metal phosphates were used as catalysts (*1*) and yielded an order of activity Cu(II) > Cd(II) > Zn(II) for

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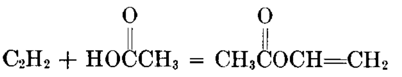
TABLE 1
SOME HETEROGENEOUSLY CATALYZED REACTIONS OF ACETYLENE AND TYPICAL CATALYSTS

Reaction	Typical catalysts
$C_2H_2 + HCl = C_2H_3Cl$	Supported chlorides of Hg(II), Bi(III), Cd(II), Zn(II)
$C_2H_2 + HOH = CH_3CHO$	Phosphates, tungstates, and molybdates of Cu(II), Cd(II), Zn(II); CdO; ZnO
 $C_2H_2 + HO\overset{\overset{O}{\|}}{C}CH_3 = CH_3\overset{\overset{O}{\|}}{C}OCH{=}CH_2$	Cadmium and zinc silicates; Hg(II) phosphates; supported Bi(III), Hg(II), Cd(II), and Zn(II) acetates

the most active cations; all other metal phosphates examined showed little or no conversion. These investigators suggested that the common properties making Cu(II), Cd(II) and Zn(II) active catalysts are the dipositive charge, stability with respect to reduction by acetylene, and the electron configuration. The configurations of the outermost subshells of these cations are Cu(II), $3d^9$; Zn(II), $3d^{10}$; and Cd(II), $4d^{10}$. Gorin and Gorn (*1*) concluded that the C_2H_2–H_2O reaction mechanism involves "activation" of the C_2H_2 by formation of a polar complex with the metal cations at the catalyst surface. The same investigators (*2*) examined the effect of anion in the catalytic hydration of C_2H_2; although phosphates, tungstates, and molybdates were most active, they concluded that the effect of anion is secondary, influencing mainly the distribution of reaction products. The inactivity of certain compounds, such as those of calcium, was ascribed to the inability of that cation to form the hypothetical acetylene–metal complexes.

The vapor-phase hydrochlorination of C_2H_2 has received considerable attention. Wibaut and van Dalfsen (*3*) examined this reaction over a series of silica-supported metal chlorides. Arranged in order of decreasing activity toward conversion of acetylene to vinyl chloride, the catalysts were the chlorides of Hg(II), Bi(III), Zn(II), and Fe(III). Zn(II) was most reactive toward the formation of the by-product 1,1-dichloroethane, however. Patat and Weidlich (*4*) studied the rate of the hydrochlorination reaction over a series of metal chlorides supported on carbon and on clay. The catalysts, arranged in order of decreasing reaction rate observed, were the chlorides of Hg(II), Pt(IV), Hg(I), Cu(II), Fe(III), and Ba(II). Several papers by Gel'bshtein and co-workers (*5*, *6*, *7*) report the results of a volumetric study of the hydrochlorination of C_2H_2 over metal chlorides supported on charcoal. The adsorption capacity for C_2H_2 followed the same sequence as the catalytic activity: Hg(II) > Bi(III) > Cd(II) > Zn(II). On the basis of this and their measured equilibrium constants for metal–acetylene and metal chloride complex formation, the rate-determining step for the hydrochlorination was assumed to be

$$MeCl_n{\cdot}C_2H_2 + HCl \rightarrow MeCl_n{\cdot}C_2H_2{\cdot}HCl$$

The vapor-phase reaction of C_2H_2 and acetic acid, catalyzed by carbon-supported metal acetates, was examined by Vasil'eva and co-workers (*8*). The cations of the most active metal acetate catalysts, arranged in order of decreasing rate constants for the formation of vinyl acetate, were Hg(II) > Cd(II) > Zn(II) ~ Ni(II). On the basis of the kinetics observed, the reaction mechanism was proposed to have as a slow step the complexation of metal acetate with acetylene.

$$Me(CH_3COO)_n + C_2H_2 \rightleftharpoons Me(CH_3COO)_n{\cdot}C_2H_2$$

In summary, the data available for vapor-phase catalytic reactions of C_2H_2 and HQ suggest that

(1) the most effective catalysts are those containing metal ions with filled *d* subshells, and

(2) intermediates in reactions of this type are metal–acetylene complexes.

The present work was undertaken to investigate, by means of the more direct infrared method (*9*, *10*), the correlations of previous investigators concerning the activity of catalysts for C_2H_2–HQ reactions. It was hoped that a determination of the structure and bonding of chemisorbed acetylene would reveal the basis of any correlation between the chemisorbed state and catalytic activity of the adsorbent. The specific approach was to (1) observe the infrared spectra of acetylene adsorbed on some silica-supported metal chlorides, (2) determine the activity of the same materials as catalysts toward the hydrochlorination of acetylene, and (3) attempt to correlate the infrared bands observed with the order of catalytic activity. If nothing else, the results should aid in determining to what extent differences in adsorbed species observed by infrared spectroscopy are related to differences in catalytic activity for C_2H_2–HQ reactions.

EXPERIMENTAL

Infrared Studies

Apparatus. The infrared spectrometer used was a Perkin-Elmer Model 12C (single beam) with sodium chloride prism. The instrument was modified in the manner described by Eischens (*9*); the source unit was moved to a vertical position and a mirror system (lower source unit) was constructed to focus the radiation on the monochromator entrance slit. The entire optica path was purged continuously with dry purified N_2.

The sample cell (Fig. 1), supported vertically between the upper and lower source unit windows, was made from 20 cm by 5 cm Pyrex tubing. CaF_2 windows were sealed, with a silica (Cab-O-Sil)–fluorosilicone grease mixture, to glass rings bonded to the cell ends with Glyptal cement. A thermocouple was sealed into the cell wall with its junction at the sample site. Samples were supported at the focal point of the infrared beam on a Pyrex tripod. The cell heater consisted of beaded resistance wire covered with asbestos. The CaF_2 windows were cooled by a flow of dry compressed air directed over the cell ends through perforated copper tubing. A sidearm and joint provided connection to a vacuum system, by means of which dynamic vacua to 10^{-6} torr could be obtained at room temperature with solid samples in the cell. Pressures in the range 760–1 torr were measured with a diaphragm gauge, in the range 1–10^{-3} torr with a thermocouple gauge, and below 10^{-3} torr with an ionization gauge.

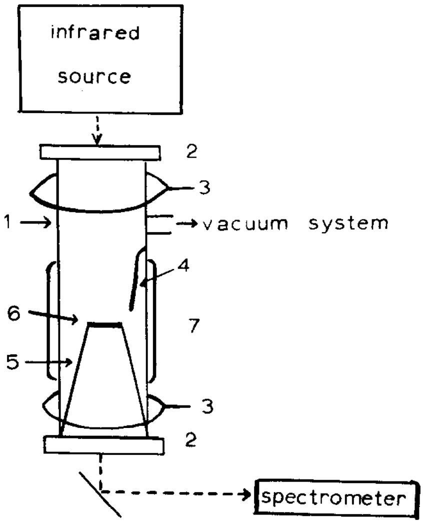


FIG. 1. Diagram of the infrared cell: (1) 5-cm ID Pyrex tubing; (2) CaF_2 windows; (3) cooling rings; (4) thermocouple; (5) glass tripod; (6) sample wafer; (7) heater.

Reagents. Commercial acetylene (>96%) was purified by successive passage through pyrogallol, concentrated H_2SO_4, soda lime, and $CaCl_2$, followed by fractionation in a vacuum system. After pumping on the solid at liquid nitrogen temperature for several hours, the middle fraction of the boiling liquid was collected in a previously evacuated bulb. Infrared and mass spectra of the gas showed it to be more than 99% pure.

Propyne was passed through drying towers into a vacuum system, solidified and pumped for several hours at liquid nitrogen temperature. Any remaining acetylene impurity was removed by briefly pumping on the liquid phase; again the middle fraction was collected. Only a trace (< 1%) of C_2H_2, as evidenced by the ν_5 band, could be detected in the infrared spectrum of the gas.

Silica-supported metal chlorides were prepared by stirring dilute hydrochloric acid solutions of reagent grade metal chlorides with a predetermined quantity of Cab-O-Sil HS-5 (Cabot Corp., Boston, Massachusetts) to produce a catalyst composition of 0.1 mole metal chloride per 100 g catalyst. These materials were dried at 200°C until use. Cab-O-Sil HS-5 is a pyrogenic silica of surface area 300–350 m^2/g with particle size of about 0.01 μ. Surface area measurements by low-temperature nitrogen adsorption averaged 240 m^2/g after the impregnation. Some catalysts were prepared with Davison 01 Grade silica gel as a support, for reasons given below, and yielded the same infrared results.

Procedures. Samples were made in pellet form by pressing in a 1-inch diameter die at a pressure of 12 700 lb/sq inch. The pellets used had an average mass of 0.23 ± 0.02 g; the average "optical thickness" was 0.045 ± 0.004 g/cm^2. Samples were mounted in the cell which was subsequently evacuated with mild heating (150°C) to below 10 μ the diffusion pump turned on, and the cell temperature raised to 350°C; most water then had been removed. After evacuation for 1 hr at 350°C, the cell was cooled to room temperature and a background spectrum taken. Instrumental parameters were adjusted to yield maximum resolution in all spectral regions of interest. Purified acetylene or propyne was admitted to the system at a pressure of 1 torr and a spectrum taken under the same instrumental conditions. A further spectrum was taken generally after an hour of contact of gas with catalyst. The cell was then evacuated to 10^{-5} torr and a spectrum taken to qualitatively examine the strength of adsorption. Further programmed evacuations and heating yielded information as to the strength of chemisorption in some cases.

At least three experiments were carried out for each adsorption study to check reproducibility of the spectra; reproducibility was within ± 2–3 cm^{-1}. Spectral shifts cited are from comparison with gas-phase spectra obtained with the modified Perkin-Elmer 12 C using the same cell.

Catalyst Activity Studies

Apparatus. The reaction system used in experiments to measure the relative activities of silica-supported metal chlorides for the hydrochlorination of acetylene was of the flow type and is diagrammed in Fig. 2. All joints were sealed with Apiezon W wax and all stopcocks were of the pressure type. The catalysts temperature was determined using an iron-constantan thermo-

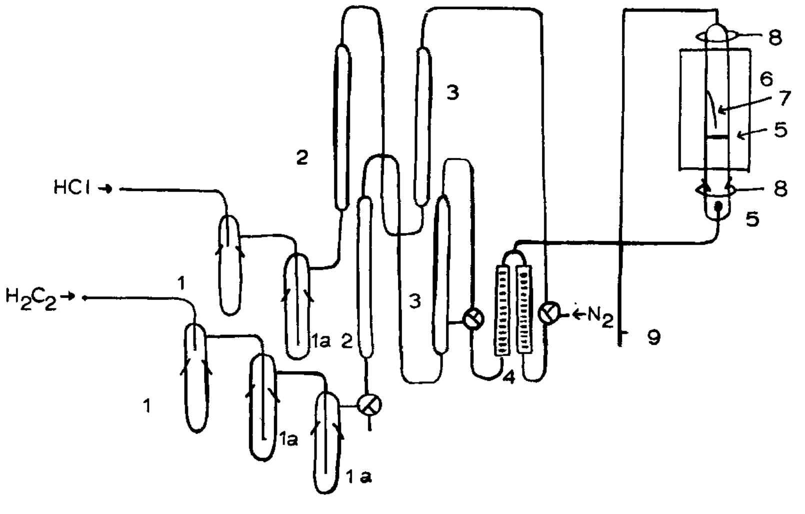


FIG. 2. Flow system for catalyst activity studies: (1) traps; (1a) H_2SO_4 traps; (2) indicating silica gel; (3) $CaCl_2$; (4) flow meter; (5) glass frit; (6) furnace; (7) thermowell; (8) cooling rings; (9) outlet with surgical rubber tip; ⊗ , three-way stopcocks; ↓↑, standard taper joints.

couple in a thermowell positioned in the catalyst bed. Flow rates of C_2H_2 and HCl were precisely measured with F1100 flow meters from Roger Gilmont Instruments, Inc.

A Gow-Mac vapor-phase chromatograph equipped with a 10-mV recorder was used for the analysis of exit gases. An 18-ft column of silicone SE-30 (Wilkens Instrument and Research, Inc.) supported in Fluoropak 80, nonpolar, 40–60 mesh (Fluorocarbon Co.) gave excellent separation of C_2H_2, HCl, and C_2H_3Cl.

Reagent. Research grade hydrogen chloride and acetylene were purified by passage through sulfuric acid traps and drying tubes of indicating silica gel and calcium chloride.

The catalysts were prepared by the impregnation procedure described above to yield a composition of 0.1 mole/100 g catalyst, on Davison Grade 01 silica gel previously purified by steam treatment. This silica initially has a specific surface of 450 m^2/g with average particle size of 3–8 mesh; after impregnation the specific surfaces averaged 430 m^2/g. For reaction studies all material was used which did not pass through a 40-mesh screen after the impregnation treatment and drying. This support, rather than the Cab-O-Sil, was used because of its superior physical characteristics; no success was achieved in maintaining uniform flow rates with the Cab-O-Sil supported catalysts.

Procedures. Sixty ml of catalyst was placed in the reactor, the bed being supported by the fritted glass. The catalyst was heated in flowing nitrogen, to simulate vacuum conditions, for 5 to 10 hr at 200°C. While regulating the temperature to 181°C, HCl was passed over the catalyst; this pretreatment was from 15 to 30 min long. Time zero was marked as the beginning of C_2H_2 flow. The calculated flow rate of C_2H_2 was 62.7 ml/min and that of HCl was 47.0 ml/min; these rates were verified experimentally by passage over the SiO_2 support. Exit gas samples were analyzed at 15-min intervals.

X-Ray diffraction patterns and carbon analyses of all catalysts were obtained before and after reaction.

RESULTS AND DISCUSSION

Infrared Studies

Infrared spectra of acetylenes adsorbed on silica-supported $CaCl_2$, $MnCl_2$, $CuCl_2$, and $ZnCl_2$ were obtained to test the validity of the hypothesis that only those catalysts whose cations have filled *d* orbitals are active catalysts for the addition of HQ compounds to acetylene. From available data on these reactions, the formation of metal–acetylene complexes as intermediates is indicated. This implies that the filled *d* orbitals play an important role in such complex formation and, therefore, in the catalysis. The cations chosen are examples of vacant 3*d* orbitals, Ca(II); half-filled 3*d* orbitals, Mn(II); and filled 3*d* orbitals, Zn(II). Copper(II), $3d^9$, was investigated because its salts have been shown to be active catalysts.

SiO_2. Yates and Lucchesi (11) have shown that acetylene interacts, if at all, very weakly with silica. The adsorption of acetylene and propyne on Cab-O-Sil, prepared and treated exactly as the supported metal chlorides, was examined to verify their result. No evidence of chemisorbed acetylene or propyne was observed in the infrared spectra using the techniques described under Experimental. This demonstrates not that silica has no effect on the interaction of gas with the metal chlorides, but that any adsorption of acetylene or propyne observed by infrared is dependent upon the presence of the metal chloride.

$CaCl_2$-SiO_2. The adsorption of C_2H_2 on $CaCl_2$-SiO_2 yielded only one infrared band characteristic of adsorbed species. The spectrum is qualitatively so similar to that for C_2H_2 adsorbed on $ZnCl_2$-SiO_2 (Fig. 5), that it is not shown. (The band at 3650 cm^{-1}, observed for all samples, is residual–OH.) The single band is observed at 3225 cm^{-1} for $CaCl_2$-SiO_2, does not change on standing for 40 min, and has a relative intensity* of 14%. After evacuation at 10^{-5} torr for 10

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* The band intensities reported throughout this work are without fundamental significance. Reported intensities are band depths in percent of the total scale, and are used only to determine whether the concentration of a given species changes with time.

min no absorption at 3225 cm^{-1} was visible, indicating weak chemisorption.

It may be assumed that the band at 3225 cm^{-1} is due to a normal vibration since combination bands usually are of lesser intensity and it is unlikely that a combination band of this intensity would be the only one appearing for an adsorbed species. There are two normal vibrations of C_2H_2 having frequencies in this region (*12*). One is the asymmetric ≡C–H vibration, ν_3, observed in the gas phase at 3285 cm^{-1}. The other is the symmetric ≡C–H vibration, ν_1, which is infrared inactive but is observed in the Raman spectrum at 3374 cm^{-1}. When acetylene is monosubstituted, resonance between the two ≡C–H groups is removed, and only ν_1 remains. At the same time, the reduced mass of the molecule with respect to vibration of the ≡C–H bond is increased and the frequency of ν_1 decreases. If the single band at 3225 cm^{-1} were due to the ν_1 vibration, the symmetry of C_2H_2 would be reduced in the adsorbed state, probably corresponding to monosubstitution; the axis of the acetylene–surface atom bond would coincide with the axis of the acetylene molecule. Such a species could be formed by loss of a hydrogen ion by C_2H_2 and overlap of the filled *sp* hybrid of C_2H^- with the vacant 4*s* orbital of a calcium ion. Such a species would be strongly chemisorbed, however, and this is not consistent with the ease of removal of the adsorbed species by evacuation. Further, although not definitive because of the possible low intensity of the absorption, the –C≡C– vibration, ν_2, is not observed. If, on the other hand, the absorption at 3225 cm^{-1} is due to the ν_3 vibration the C_2H_2 must retain its symmetry; the axis of the acetylene–surface atom bond must be perpendicular to the axis of the acetylene molecule. Such a species could be formed by overlap of the filled π-bonding orbital of C_2H_2 with the vacant 4*s* orbital of the calcium ion. Bonds of this type will be referred to as μ-bonds (*13*).

With the exception of the absence of the ν_2 band, none of the foregoing arguments excludes the possibility that a species adsorbed normal to the surface could be formed by hydrogen bonding. If the observed band were due to ν_1, however, the shift from its gas-phase frequency would be −150 cm^{-1}. Wilmshurst (*14*) has shown that the frequency of ν_1 in H–C≡C–X molecules is insensitive to changes in the mass of X. His calculations show that as the mass of X is varied from 1 amu to 1000 amu, ν_1 decreases less than 40 cm^{-1}. A shift of −150 cm^{-1} cannot be explained by hydrogen bonding. If the 3225-cm^{-1} band is due to ν_3, the shift relative to the gas-phase frequency is −65 cm^{-1}. This is easily explained as due to the reduction in bond order of –C≡C– resulting from μ-bonding to a surface calcium ion. (The $\overset{\diagdown}{=}$C–H frequency is 3020 cm^{-1}, about 270 cm^{-1} lower than the ≡C–H frequency.)

The probable surface species producing the 3225-cm^{-1} band is μ-bonded C_2H_2; this structure is represented in Fig. 3, only one π-bonding orbital of C_2H_2 being shown to simplify the diagram.

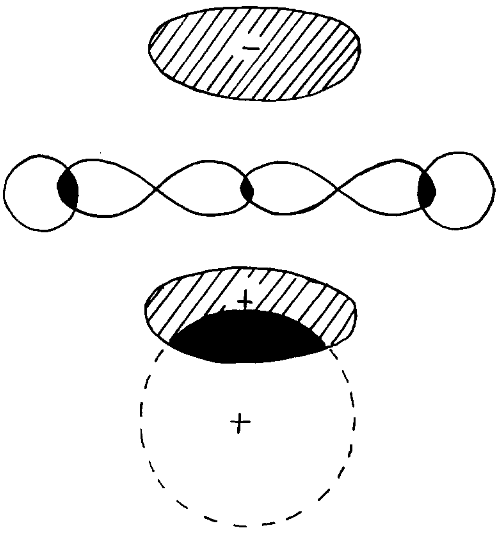
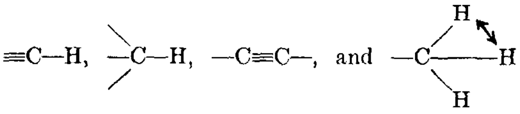


FIG. 3. A simplified representation of orbital interactions in a μ-bonded adsorbed alkyne.

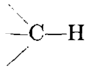
Because of this assumed μ-bonding of chemisorbed acetylene, it was of interest to observe the changes in the properties of the acetylene triple bond on adsorption to better delineate the role of π-electrons in the C_2H_2–catalyst interaction. Propyne, whose –C≡C– vibration is infrared-active, was adsorbed in experiments identical to those performed with acetylene.

Absorption bands in the spectrum of propyne adsorbed on $CaCl_2$-SiO_2 were qualitatively the same as those observed for propyne on $ZnCl_2$-SiO_2 (Fig. 6), and a separate spectrum is not shown. The absorption band frequencies due to adsorbed propyne species on $CaCl_2$-SiO_2 were 3292, 2955, 2105, and 1446 cm^{-1}. Neither the frequencies nor intensities changed on standing, indicating no observable change in chemisorbed species. Most of the adsorbed propyne was removed by evacuation for 10 min. This set of frequencies roughly corresponds to the four normal vibrations of gas-phase propyne observed in the 4000-1400 cm^{-1} range. These are the ν_1, ν_2, ν_3, and ν_7 vibrations observed at 3345, 2955, 2134, and 1458 cm^{-1}, respectively, in the gas phase. The absorption bands of adsorbed propyne are assumed to arise from this set of normal vibrations. They are characteristic of the



vibrational frequencies and their average shifts relative to the gas phase are −52, 0, −29, and −12 cm^{-1}, respectively. The spectral data indicate that the adsorbed species is an essentially unchanged propyne molecule. Interactions satisfying this requirement are μ-bonding of propyne to a calcium ion or hydrogen bonding through the ≡C–H to a chloride ion. The hydrogen-bonded structure can be dismissed on the basis that the substitution of –H by a grouping of larger mass increases the frequency of the –C≡C– vibration; the –C≡C– frequency of CH_3–C≡C–CH_3, for example, is 2233 cm^{-1}, about 90 cm^{-1} higher than that of propyne.

The observed frequencies are consistent with a μ-bonded species. Overlap of a propyne π-bonding orbital with a vacant calcium 4*s* orbital would reduce the –C≡C– bond order, lowering both the –C≡C– and ≡C–H frequencies (*15*). The observation of no shift for the



frequency is consistent with the fact that the methyl group is removed from the propyne–surface bond. The methyl bending vibration, occurring in the spectral region where frequencies can be measured with highest precision, shows a −12-cm^{-1} shift; thus the –CH_3 group does appear to be somewhat affected by bonding because of steric or inductive effects. The surface species for propyne adsorbed on $CaCl_2$-SiO_2 is therefore analogous to that formed by acetylene.

$MnCl_2$-SiO_2. The spectrum of acetylene adsorbed on $MnCl_2$-SiO_2 contains a band at 3228 cm^{-1}, the only band characteristic of adsorbed species. No changes in frequency or intensity were observed after 30 min, and after 10 min of evacuation the band is barely observable. These data are exactly analogous to those from C_2H_2 adsorption on $CaCl_2$-SiO_2, and the observed absorption is assumed due to the ν_3 vibration of a symmetric C_2H_2 molecule. The shift of ν_3 from its gas phase frequency is −62 cm^{-1}.

The outer electron configuration of Mn^{2+} is $3d^5$ but, because it is difficult to predict the type and degree of *d* orbital splitting in this surface environment, it will be assumed that the vacant orbital most likely to bond is the 4*s*. Again, it is assumed that μ-bonding occurs by overlap of this 4*s* with an acetylene π-bonding orbital. In this case, however, the populated 3*d* orbitals of Mn(II) may overlap with an acetylene π-antibonding (π*) orbital to form a π-bond. The postulation of such π-bonding in a number of olefin and acetylene complexes (*16*, *17*, *18*) and chemisorbed species (*19*) indicates this possibility, although its contribution to the total bond strength of the adsorbed species will depend greatly upon the relative distances between lobes of the π* and 3*d* orbitals. Both the μ-bond and the π-bond tend to decrease the bond order of –C≡C–; the μ-bond by removing charge density from the internuclear region, and the π-bond by increasing the charge density of the π*-orbital.

A possible simplified orbital diagram of acetylene adsorbed on a silica-supported metal chloride, where conditions exist for

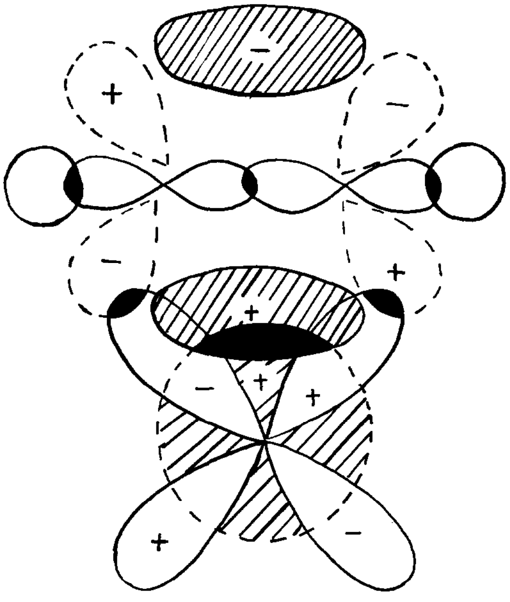
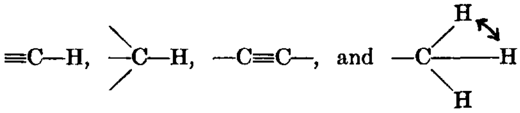


FIG. 4. A simplified representation of a μ- and π-bonded adsorbed alkyne.

π-bonding of the type discussed, is shown in Fig. 4.

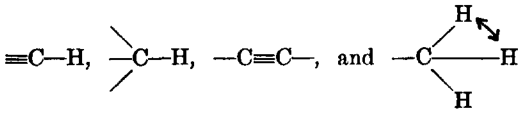
The spectrum of $MnCl_2$-SiO_2 in the presence of propyne shows the same general features as the spectum of propyne adsorbed on $CaCl_2$-SiO_2. The bands characteristic of adsorbed propyne occur at 3295, 2960, 2090, and 1446 cm^{-1}. The observable surface species is an essentially unchanged propyne molecule with absorption of the


$\equiv C\text{—}H,\quad {>}C\text{—}H,\quad \text{—}C\equiv C\text{—},\quad \text{and}\quad \text{—}C(H)(H)\text{—}H$

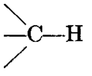
frequencies shifted by −50, +5, −44, and −12 cm^{-1}, respectively. A μ-bonded and π-bonded species analogous to that of C_2H_2 on $MnCl_2$-SiO_2 is consistent with these shifts.

$ZnCl_2$-SiO_2. A typical spectrum of $ZnCl_2$-SiO_2 in the presence of C_2H_2 is shown in Fig. 5. As with the $CaCl_2$-SiO_2 and $MnCl_2$-SiO_2 systems, one band ascribed to chemisorbed C_2H_2 is observed. The frequency of this band is 3222 cm^{-1}. No changes in frequency or intensity are observed after 30 min, and a small absorption remains after 40 min of evacuation. The 3222-cm^{-1} absorption is by the ν_3 vibration of a symmetric C_2H_2 molecule, with a −68-cm^{-1} shift from the gas-phase frequency. The C_2H_2 is μ-bonded and π-bonded to zinc(II), as in the $MnCl_2$-SiO_2 case; this bonding is depicted by Fig. 4.

A spectrum of $ZnCl_2$-SiO_2 in the presence of propyne is shown in Fig. 6. In addition to the usual –OH band at 3650 cm^{-1}, four absorption bands characteristic of adsorbed species are observed which correspond to the four normal vibrations of propyne gas in the 4000-1400 cm^{-1} region. No change in the frequencies or intensities are observed after 30 min, and some adsorbed propyne remains after evacuation for 200 min. The absorption frequencies are at 3275, 2950, 2073, and 1443 cm^{-1} and correspond to the


$\equiv C\text{—}H,\quad {>}C\text{—}H,\quad \text{—}C\equiv C\text{—},\quad \text{and}\quad \text{—}C(H)(H)\text{—}H$

vibrations. These frequencies represent shifts compared with the gas phase of −70, −5, −61, and −15 cm^{-1}. The data are analogous to those obtained from $CaCl_2$-SiO_2 and $MnCl_2$-SiO_2 in the presence of propyne. In this case, the propyne is μ-bonded and π-bonded to zinc(II), and the bonding diagram is again represented by Fig. 4. The μ-bond and π-bond, as in the case of $MnCl_2$-SiO_2, significantly lower both the –C≡C– and ≡C–H frequencies. The


${>}C\text{—}H$

frequency shift is small; the methyl bending frequency shift of −15 cm^{-1} reveals (as in other cases) the small interaction of the methyl group.

$CuCl_2$-SiO_2. The spectrum of $CuCl_2$-SiO_2 after the addition of C_2H_2 is shown in Fig. 7. The bands identified with adsorbed acetylene appear at 3290, 3205, and 1818 cm^{-1}. The lower frequency shoulder on the 3650-cm^{-1} –OH band represents the appearance of a new –OH species. The adsorbed acetylene bands are assumed characteristic of a single adsorbed species because of subsequent behavior. After 34 min, the

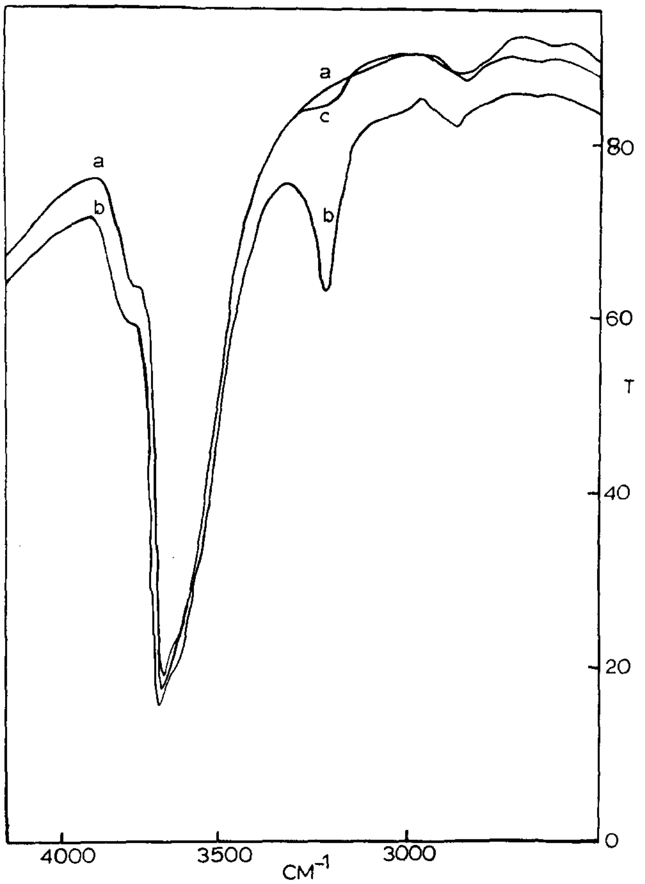
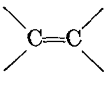


FIG. 5. Infrared spectrum of acetylene adsorbed on silica-supported zinc chloride: a, catalyst after treatment at 350°C for 1 hr at 10^{-5} torr; b, after addition of 1 torr C_2H_2 at 25°C; c, after evacuation at 10^{-5} torr.

–OH frequency increased roughly twice in intensity while the acetylene bands decreased 10–20% in intensity during the same period. Evacuation at 10^{-5} torr ultimately reduced the acetylene band intensities by 60–70 %. The bands at 3290 and 3205 cm^{-1} are in the $\equiv$C–H frequency region and are assigned to the ν_1 and ν_3 vibrations, respectively. The band at 1818 cm^{-1} lies between the –C$\equiv$C– frequency of gas-phase acetylene and the



frequency at 1650 cm^{-1} (*14*); this band is assigned to the ν_2 vibration. The shifts relative to the gas phase are -84, -85, and -156 cm^{-1} for the ν_1, ν_3, and ν_2 vibrations, respectively. The existence of both ν_1 and ν_3 vibrations in adsorbed acetylene is evidence that one $\equiv$C–H group is not strongly interacting with the surface.

The data are well explained by acetylene μ- and π-bonded to copper(II). Since the outer electron configuration of Cu(II) is $3d^9$, an acetylene π-bonding orbital may overlap with the vacant $4s$ while a half-filled $3d_{yz}$ or $3d_{zx}$ orbital overlaps with an acetylene π^*-orbital. This structure would be represented by the diagram in Fig. 4. The interaction is apparently strong enough that the symmetric vibrations ν_1 and ν_2 become infrared-active due to reduction in symmetry of the C_2H_2 molecule. The strong bond formed by μ- and π-bonding in this case decreases the bond order of –C$\equiv$C– sufficiently to account for the large shifts to lower frequency. The only difference between this surface species and those ob-

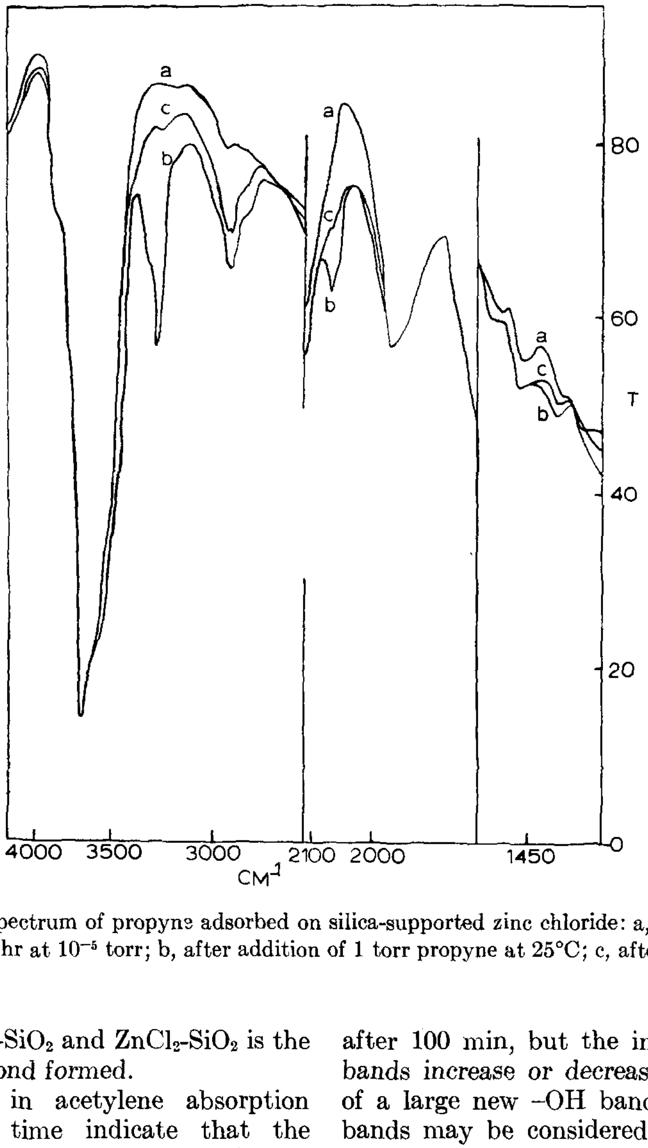


Fig. 6. Infrared spectrum of propyne adsorbed on silica-supported zinc chloride: a, catalyst after treatment at 350°C for 1 hr at 10^{-5} torr; b, after addition of 1 torr propyne at 25°C; c, after evacuation at 10^{-5} torr.

served on $MnCl_2$-SiO_2 and $ZnCl_2$-SiO_2 is the strength of the bond formed.

The decrease in acetylene absorption intensities with time indicate that the μ- and π-bonded species is decreasing in concentration. The simultaneous increase in –OH concentration was the only other spectral change observed in the 4000–1400 cm^{-1} region. A reasonable explanation is the formation of carbide species such as CuC_2 through the transfer of hydrogen ions to the silica support thereby increasing the –OH.

The spectrum of $CuCl_2$-SiO_2 after the addition of propyne is shown in Fig. 8. The frequencies of the bands identified with adsorbed propyne are 3247, 2953, 2240, 1964, and 1437 cm^{-1}. The frequencies of these bands do not change significantly after 100 min, but the intensities of some bands increase or decrease. The formation of a large new –OH band is evident. The bands may be considered in three groups, those whose intensities increase on standing, –OH and 2240 cm^{-1}; those whose intensities decrease on standing, 3247 and 1964 cm^{-1}; and those whose intensities do not change, 2953 and 1437 cm^{-1}.

The absorptions at 3247 and 1964 cm^{-1} which decrease in intensity on standing are both assumed to be characteristic of the same surface species. These bands are assigned to $\equiv$C–H and –C$\equiv$C– vibrations and are shifted from their gas-phase values by −98 and −170 cm^{-1}, respectively. This surface species is apparently transformed on standing into a species which absorbs at

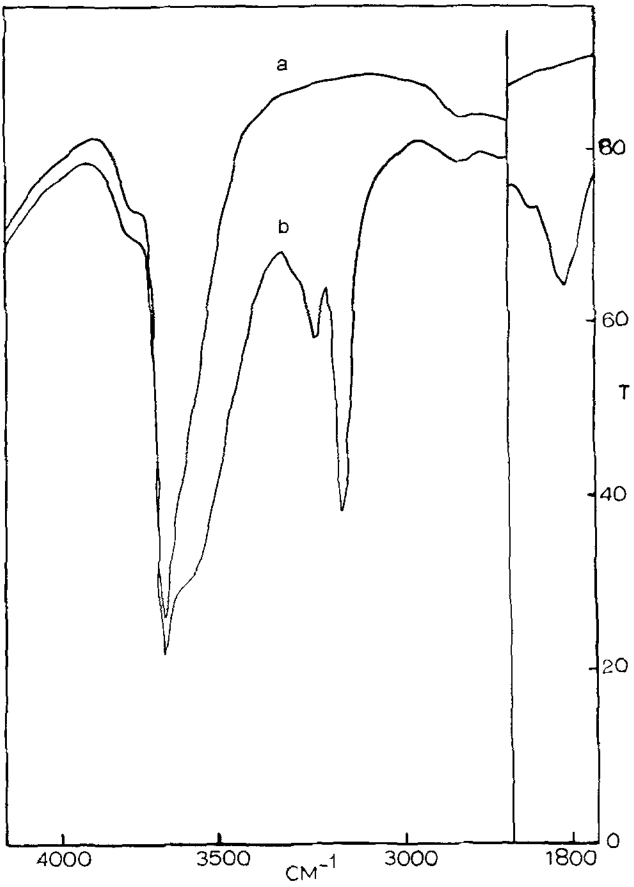
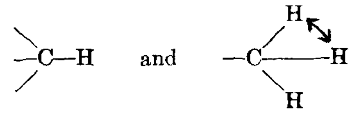


FIG. 7. Infrared spectrum of acetylene adsorbed on silica-supported copper(II) chloride: a, catalyst after treatment at 350°C for 1 hr at 10^{-5} torr; b, after addition of 1 torr C_2H_2 at 25°C.

2240 cm^{-1}. This band increases in intensity on standing and is assumed to be characteristic of the $-C{\equiv}C-$ vibration of the new surface species. A simultaneous increase occurs in the breadth of the -OH absorption at 3650 cm^{-1}. The bands at 2953 and 1437 cm^{-1} are assigned to the



vibrations, respectively. Their intensities do not change on standing and they must be characteristic of both types of adsorbed species.

The surface species with ν_1, ν_2, ν_3, and ν_7 vibrations at 3247, 2953, 1964, and 1437 cm^{-1}, respectively, is analogous to the propyne surface species observed on $ZnCl_2$-SiO_2 and $MnCl_2$-SiO_2. In this species propyne is μ-bonded and π-bonded to a copper ion. The overlapping orbitals are analogous to those in the acetylene-copper(II) surface complex. The intensities of the bands characteristic of this species which remain after 40 min of evacuation indicate that propyne is more difficult to remove from this surface than from the surfaces of $CaCl_2$-SiO_2, $MnCl_2$-SiO_2, and $ZnCl_2$-SiO_2.

For the surface species whose $-C{\equiv}C-$ vibration is at 2240 cm^{-1}, the band has been shifted +106 cm^{-1} from the gas phase. This shift indicates removal of the coupling between the $-C{\equiv}C-$ and ${\equiv}C-H$ vibrations by increase in the mass of the ${\equiv}C-H$ end of the propyne molecule. The $-C{\equiv}C-$ frequency in $CH_3-C{\equiv}C-CH_3$, for

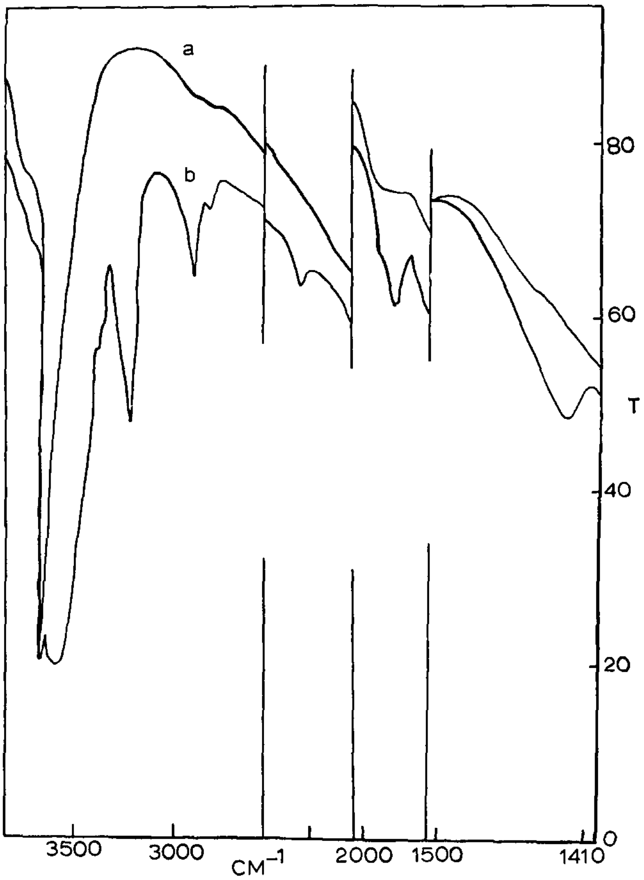
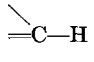


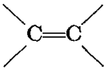
FIG. 8. Infrared spectrum of propyne adsorbed on silica-supported copper(II) chloride: a, catalyst after treatment at 350°C for 1 hr at 10^{-5} torr; b, after addition of 1 torr propyne at 25°C.

example, is 2233 cm^{-1} (*20*). No $\equiv$C–H frequency characteristic of this adsorbed species is observed. This fact, together with the observed increase in –O–H on standing, suggests that this species is formed by dissociation of the μ-bonded and π-bonded propyne into CH_3–C$\equiv$C$^-$ and H$^+$ (which forms a new surface –OH). The anion probably forms a σ-bond with a copper(II) ion by overlap of the filled *sp* hybrid orbital with the vacant 4*s* orbital of the copper(II) ion. A π-bond may also be formed by overlap of a half-filled copper(II) $3d_{yz}$ or $3d_{zx}$ orbital with a π^*-orbital of propyne. It is also possible that copper(II) is reduced to copper (I). The surface species might be represented by the diagram in Fig. 9. The concentration of this species cannot be decreased with continued evacuation.

After evacuation, a weak absorption at 3010 cm^{-1} is observed. This band is obscured by the presence of the strong ν_2 absorption at 2953 cm^{-1} and becomes distinguishable only after the diminution of the 2953-cm^{-1} band. The 3010-cm^{-1} band is characteristic of the



stretching vibration, appearing at about 3020 cm^{-1} for gas-phase molecules (*15*). The species producing this absorption may be adsorbed olefin formed by reaction of propyne with the surface. No absorption characteristic of



was observed, but this would be weak and

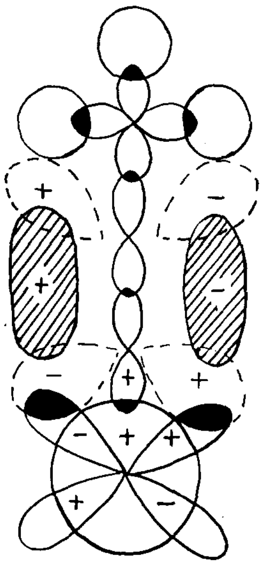
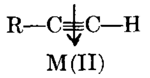


Fig. 9. A simplified representation of orbital interactions in the surface species $H_3C{-}C{\equiv}C{-}Cu^+$.

would appear in a region of intense silica bands.

Summary discussion of infrared results. Surface species observed and interpreted from infrared spectra, and frequency shifts from the corresponding gas-phase modes, for acetylene and propyne adsorbed on silica-supported $CaCl_2$, $MnCl_2$, $ZnCl_2$, and $CuCl_2$ are summarized in Table 2. The following species is common to all of the silica-supported metal chlorides investigated, where -R is -H and $-CH_3$:



$$\underset{\mathrm{M(II)}}{\mathrm{R{-}C}\overset{}{\underset{\downarrow}{\equiv}}\mathrm{C{-}H}}$$

This will be referred to as the parallel-bonded surface species, where the alkyne–metal bond is a combination of μ- and π-bonding.

For acetylene the only infrared absorption observed, common to all the parallel-bonded species, is the asymmetric ≡C-H stretching vibration, ν_3. The shifts of this vibration to lower frequency are assumed the result of the μ- and π-bonding between acetylene and the surface cation, which result in a reduction in the $-C{\equiv}C-$ bond order and decrease in ≡C-H frequency. The ≡C-H shifts, relative to the gas phase, for acetylene

TABLE 2

Surface Species and Frequency Shifts from Gas-Phase Values for Alkynes Adsorbed on Silica-Supported Metal Chlorides

Cation:	Ca(II)	Mn(II)	Cu(II)		Zn(II)
Acetylene surface species:	$\underset{\mathrm{Ca(II)}}{\mathrm{H{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$	$\underset{\mathrm{Mn(II)}}{\mathrm{H{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$	$\underset{\mathrm{Cu(II)}}{\mathrm{H{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$	CuC_2(?)	$\underset{\mathrm{Zn(II)}}{\mathrm{H{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$
Vibrational mode (cm^{-1})					
$\Delta\bar{\nu}_1$, ≡C—H	—	—	−84	—	—
$\Delta\bar{\nu}_2$, —C≡C—	—	—	−156	—	—
$\Delta\bar{\nu}_3$, ≡C—H	−65	−62	−85	—	−68
Propyne surface species:	$\underset{\mathrm{Ca(II)}}{\mathrm{CH_3{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$	$\underset{\mathrm{Mn(II)}}{\mathrm{CH_3{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$	$\underset{\mathrm{Cu(II)}}{\mathrm{CH_3{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$	$CH_3{-}C{\equiv}C{-}Cu^+$	$\underset{\mathrm{Zn(II)}}{\mathrm{CH_3{-}C}\underset{\downarrow}{\equiv}\mathrm{C{-}H}}$
Vibrational mode (cm^{-1})					
$\Delta\bar{\nu}_1$, ≡C—H	−52	−50	−98	—	−68
$\Delta\bar{\nu}_2$, $\begin{smallmatrix}\diagdown\\ -\mathrm{C}-\mathrm{H}\\ \diagup\end{smallmatrix}$	0	+5	−2		−5
$\Delta\bar{\nu}_3$, —C≡C—	−29	−44	−170	+106	−61
$\Delta\bar{\nu}_7$, $-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$	−12	−12	−21		−15
Cation electron affinity[a] (eV)	11.87	15.64	20.29	—	17.96
Cation ionization potential[a] (eV)	51.21	32	29.5	—	40.0

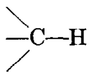
[a] Reference (*23*).

bonded to calcium, manganese, zinc, and copper ions have the order Cu(II) > Zn(II) $\simeq$ Ca(II) $\simeq$ Mn(II). The frequency measurements for adsorbed acetylene bands are not precise enough to distinguish among Zn(II), Ca(II), and Mn(II). On $CuCl_2$-SiO_2 the formation of a surface carbide is also proposed.

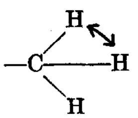
For parallel-bonded propyne the shifts of ν_1, the $\equiv$C–H stretching vibration, relative to the gas-phase frequency, show the same order of dependence on the cation as the $\equiv$C–H shifts for adsorbed acetylene. This is taken as evidence that the acetylene and propyne parallel-bonded surface species are closely analogous.

The order of –C$\equiv$C– shifts induced in parallel-bonded propyne by the cations is Cu(II) > Zn(II) > Mn(II) > Ca(II). From Table 2 it is obvious that the shifts of the –C$\equiv$C– frequencies for these surface species are separated by intervals great enough to definitely establish this order. (The observed $\equiv$C–H shift for propyne on $CaCl_2$-SiO_2 is 2 cm^{-1} greater than that observed with $MnCl_2$-SiO_2, the reverse of the order expected by comparison of the –C$\equiv$C– shifts. Little significance is attached to this because the reproducibility of measurement is $\geq$ 2 cm^{-1}.)

The apparent shifts of ν_2, the



stretching vibration, are of the same magnitude as the reproducibility of frequency measurements and are not considered significant by themselves. The shifts of ν_7, the



vibration, show some relationship to the –C$\equiv$C– shift. It appears that ν_7 shifts are the result of an inductive effect.

The infrared-active bond vibration whose frequency is most sensitive to variations in the nature of the adsorbate–surface cation interaction is the ν_3 (–C$\equiv$C–) of propyne. The extent of propyne π-cation 4*s* orbital overlap should increase with increasing electron affinity of the cation. The extent of propyne π^*-cation $3d_{yz}$ or $3d_{zx}$ orbital overlap should increase with decreasing ionization potential of the cation. A lowered –C$\equiv$C– frequency for adsorbed propyne therefore is favored by high electron affinity and low ionization potential of the cation. From Table 2, propyne –C$\equiv$C– frequency shifts are observed to increase with increasing electron affinity. No direct relationship between –C$\equiv$C– shift and ionization potential is observed. From this evidence, the μ-bonding appears to represent the more effective of the two orbital overlaps. The relative magnitudes of the electron affinities of the cations and propyne (10.56 eV) (*21*) make transfer of negative charge from propyne to cation most reasonable. It should be noted, however, that copper(II), which induces the largest shift in the –C$\equiv$C– frequency of propyne (as well as in the $\equiv$C–H frequencies of both propyne and acetylene), has both the highest electron affinity and lowest ionization potential of the cations investigated.

Analogous to the proposed formation of carbide species by acetylene on $CuCl_2$-SiO_2, replacement of $\equiv$C–H hydrogen in propyne by a surface cation appears to occur on $CuCl_2$-SiO_2.

Catalyst Activity Studies

The reaction of acetylene and HCl over silica-supported metal chlorides, where the metal ions were Hg(II), Bi(III), Zn(II), Ni(II), Cd(II), Cu(II), Mn(II), and Ca(II), was investigated at 181°C in the flow reaction system shown in Fig. 2. The principal objective was the determination of relative catalyst activities. There were serious questions about the nature of the supported metal chlorides used in previous work because of the lack of physical and chemical characterization of the materials, especially the support. Further, some of these results (*4–7*) were obtained with metal chloride catalysts supported on materials other than silica gel, and the early studies (*3*) using a silica gel support (of unknown purity and surface area) involved too few compounds to yield any correlations of catalytic activity with these infrared results.

Reaction results. Three reactions are known to have occurred over these catalysts. The principal reaction is the addition of one molecule of HCl to acetylene yielding vinyl chloride.

$$HC{\equiv}CH + HCl \rightarrow H_2C{=}CHCl$$

The second, evidenced by the formation and qualitative analysis of condensate in the reactor exit tubulation, is the addition of another molecule of HCl to give 1,1-dichloroethane, also reported by Wibaut and van Dalfsen (*3*) according to the reaction

$$H_2C{=}CHCl + HCl \rightarrow H_3CCHCl_2$$

the overall reaction in this case being

$$HC{\equiv}CH + 2HCl = H_3CCHCl_2$$

The third and more complex, indicated by the appearance of the catalysts and subsequent carbon analyses, is the formation of polymeric materials such as polyvinyl acetylenes (*22*).

$$HC{\equiv}CH + HC{\equiv}CH \rightarrow CH_2{=}CHC{\equiv}CH$$

$$CH_2{=}CHC{\equiv}CH + HC{\equiv}CH \rightarrow CH_2{=}CHC{\equiv}CCH{=}CH_2$$

$$\vdots$$

etc.

Such products have not been discussed by the previously cited workers investigating this reaction. The possibility that some "coking" could have occurred cannot be dismissed, but the formation of significant amounts of carbon seems unlikely because of the relatively low temperature.

Analysis of the gas chromatograms for unconverted acetylene and HCl in addition to the gaseous reaction product vinylacetylene allowed a quantitative comparison of the relative activities of the catalysts under the conditions cited. The results, where the formation of polymeric product as C_2 species and 1,1-dichloroethane have been accounted for, are presented in Fig. 10. The calculated percent conversions of acetylene to 1,1-dichloroethane and polymerization product, together with analytical data on the catalysts are given in Table 3. (The data for $CuCl_2$-SiO_2 are given at about 2 hr because the vinyl chloride observed had decreased to zero after 3 hr.) In all cases, most noticeably for those catalysts of higher activity, the percent conversion to vinyl chloride decreased from an initially higher value to a lower more constant value. Duplicate runs with the more active catalysts [$HgCl_2$-SiO_2, $BiCl_3$-SiO_2, and $NiCl_2$-

TABLE 3

OTHER DATA FROM CATALYTIC ACTIVITY EXPERIMENTS

Catalyst	% Conversion to dichloroethane	% Carbon on used catalyst	% Conversion to polymerization product	X-Ray analysis[a]	
				b	a
SiO_2	—	0.2%[b]	—	Amorphous	—
$HgCl_2$	0%	1.34%	3.2%	Amorphous + HgCl	Amorphous + HgCl
$ZnCl_2$	6%	4.9%	12%	Amorphous	Amorphous
$MnCl_2$	3%	1.56%	3.5%	Amorphous	—
$BiCl_3$	4%	5.0%	11%	Amorphous + BiOCl	Amorphous
$CaCl_2$	0%	0%	0%	Amorphous	—
$CdCl_2$	7%	2.31%	5.3%	Amorphous + $CdCl_2 \cdot H_2O$	—
$CuCl_2$	5%	1.7%	6.2%	Amorphous	—
$NiCl_2$	6%	2.1%	4.7%	—	Amorphous

[a] From diffraction pattern carried out before (b) and after (a) reaction.

[b] This is the carbon analysis of the unreacted support, Davison 01 silica. Other values in the table are corrected for this analysis.

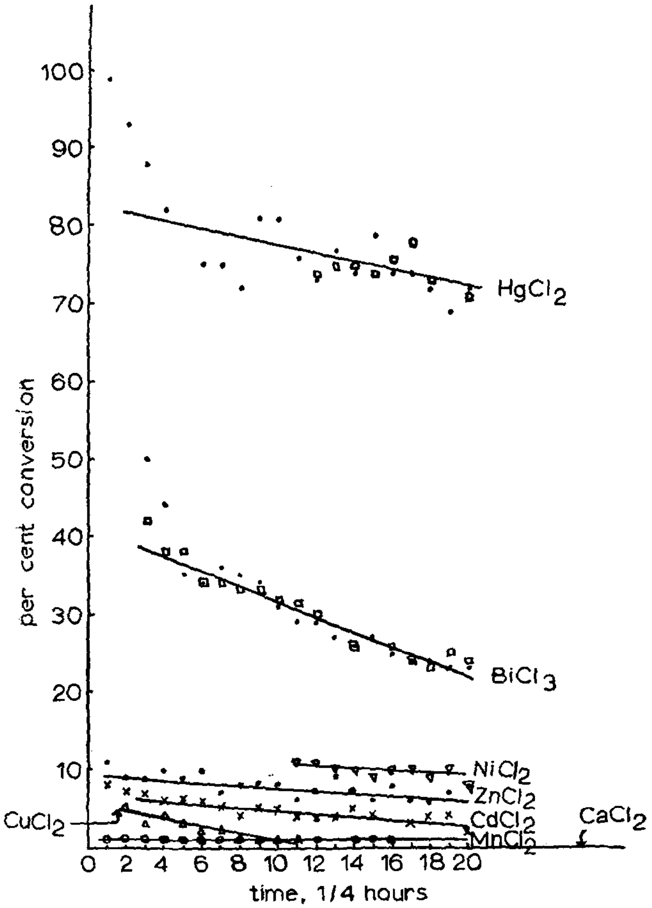


FIG. 10. Percent conversion of acetylene to vinyl chloride basis reactants as a function of time. Temperature, 181°C; silica-supported metal chloride catalysts; flow reactor.

SiO_2] are plotted to indicate the reproducibility obtained with the experimental procedure described.

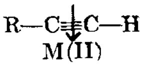
The qualitative order of catalytic activity, with the exception of $CdCl_2$-SiO_2, is the same as for those supported metal compounds which have been studied in previously cited work (*3–7*) on C_2H_2-HQ reactions. That is, in this investigation of the hydrochlorination of acetylene the order of catalytic activity of the silica-supported metal chlorides is Hg(II) > Bi(III) > Ni(II) > Zn(II) > Cd(II) > Cu(II) > Mn(II) > Ca(II).

Unlike previous studies, the activity of the $CdCl_2$-SiO_2 catalyst is lower than that of $ZnCl_2$-SiO_2; the reason is possibly revealed by the X-ray analyses (Table 3). All catalysts examined were completely amorphous except $HgCl_2$-SiO_2, $BiCl_3$-SiO_2, and $CdCl_2$-SiO_2; some amounts of particulate HgCl, BiOCl, and $CdCl_2 \cdot H_2O$, respectively, were found on these. In all studies the cadmium compounds have been found significantly lower in activity than either the corresponding bismuth(III) or mercury(II) compounds and the observation of crystalline $CdCl_2 \cdot H_2O$ suggests that the lack of uniform dispersion on the silica support placed this catalyst at a lower activity level than the $ZnCl_2 \cdot SiO_2$ catalyst for these experiments. The $HgCl_2$ and $BiCl_3$ appear to have reacted with the support and/or in solution to produce some macrocrystalline HgCl and BiOCl on the silica surface. (Several attempts to produce $HgCl_2$-SiO_2, $BiCl_3$-SiO_2, and $CdCl_2$-SiO_2 catalysts showing a completely amorphous X-ray pattern like the other materials met with no success.) To some extent, then, the quantitative catalytic activity depends upon this support. However, because of the poorly specified supports used in other catalytic activity studies cited and the general agreement in qualitative order of activity for those metal ions studied in common, the support apparently plays a secondary role at least for the most active catalysts.

It is concluded that the catalytic activity studies carried out in this work have confirmed the general order of activity for C_2H_2-HQ reactions to be Hg(II) > Bi(III) > (Zn(II) > Mn(II) > Ca(II). The catalytic activity of other metal compounds relative to the last three appear to depend upon the specific reaction and experimental conditions.

Summary and Conclusions

Acetylene and propyne were found adsorbed on silica-supported metal chlorides through μ-bonding and π-bonding with the cations. Since the μ-bonding appears to constitute the largest contribution to the adsorbate–surface bond, the charge distribution in these surface complexes is represented simply as



$$\mathrm{R{-}C}\underset{\underset{\mathrm{M(II)}}{\downarrow}}{\equiv}\mathrm{C{-}H}$$

As indicated by frequency shifts relative to the gas phase of $-C\equiv C-$ for propyne, and $\equiv C-H$ for propyne and acetylene, shown in Table 2, the order of adsorbate polarization by metal ion is Cu(II) > Zn(II) > Mn(II) > Ca(II).

The *initial* order of catalytic activity for the hydrochlorination of acetylene by the silica-supported matal chlorides is Zn(II) > Mn(II) > Ca(II), with Cu(II) in a rather uncertain position because of its rapid decline in activity. The rapid decline of $CuCl_2$-SiO_2 activity represents the removal of active sites; whether this is a result of reduction to Cu(I) or strong chemisorption of site-blocking species, such as the infrared-observed $CH_3C\equiv C-Cu$, is not known. X-ray analyses of $CuCl_2$-SiO_2 show only an amorphous material and the carbon analysis shows no unusually large buildup of polymeric material (e.g., cuprene) as compared with the other catalysts.

Although the infrared interpretations and catalytic activity data suggest that a correlation between absorption band frequency shifts of adsorbed parallel-bonded species and order of catalytic activity may exist, such a correlation is tenuous because spectral measurements were not made under actual reaction conditions. It is useful however, to suggest an interpretation of this correlation if the infrared-observed species were an intermediate in the reaction of acetylene with HCl. The polarization of the adsorbed acetylene by the surface cationic species decreases the bond order of $-C\equiv C-$, as evidenced by the infrared spectra. While it is a fact not understood, the carbon–carbon triple bond is in general less reactive toward HQ addition than is the carbon–carbon double bond. The more charge is withdrawn from the carbon–carbon internuclear region in acetylene by the surface interaction, the more reactive should be the adsorbed acetylene. This is consistent with the infrared and activity data for the $ZnCl_2$-SiO_2, $MnCl_2$-SiO_2, and $CaCl_2$-SiO_2 catalysts. (The lack of correlation for $CuCl_2$-SiO_2, less active than $ZnCl_2$-SiO_2, is not meaningful for the reason previously cited.) From this interpretation the catalytic activity of a cation would arise from its ability to polarize acetylene in the manner depicted. Catalytic activity should increase with increasing electron affinity of the cation, the most important requirement therefore being a strong μ-bond.

The relatively high activity of the $NiCl_2$-SiO_2 catalyst was unexpected on the basis of previously cited studies and their interpretations. No reported application of d^8 ion catalysts for C_2H_2-HQ reactions has been found, while basic studies and applications of Zn(II) and Cd(II) compounds are common. This result is consistent, however, with the interpretation proposed here. If the infrared-observed surface species are analogous to reaction intermediates the general requirements for an active catalyst cation are (1) the presence of a vacant orbital suitable for μ-bonding with acetylene, and (2) a high electron affinity. The presence of filled *d* orbitals, as suggested by previous work, would not be a requirement *per se* for an active catalyst cation.

Work on these systems is being continued in an effort to more rigorously correlate the infrared spectroscopic studies with catalytic activity of the same compounds. Extension of infrared studies to the more active catalysts of Hg(II), Bi(III), and Ni(II), attempted so far without definitive results because of sample physical characteristics, is important. Experiments with other silica-supported metal compounds are underway to obtain more data on the relationship between cation properties and catalytic activity for C_2H_2-HQ reactions.

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