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Infrared Spectral Observation of the Interaction of Acetone with Silica-Supported Ni and Co

G. BLYHOLDER AND D. SHIHABI

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

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Infrared spectra of the adsorbed species produced by acetone on silica-supported Ni and Co have been obtained. Contrary to previous reports acetone does chemisorb on silica-supported Ni at 25°C but the amount is small. The structure of the adsorbed species is that of acetone coordinated through the oxygen atom. There is also some decomposition to CO and hydrocarbons at 25°C. On cobalt much more acetone adsorbs with isopropoxide, coordinated acetone, acyl groups and hydrogen-deficient, carbon-containing fragments as the initial surface structures. Low hydrogen conditions favor the formation of oxygen-coordinated acetone and acyl surface species while addition of hydrogen converts acyl to coordinated acetone surface species and coordinated acetone to isopropoxide surface species as well as hydrogenating carbon-containing surface fragments. No infrared evidence was found for free OH groups of alcohols attached to the surface by metal–carbon bonds as has been previously postulated in catalytic hydrogenation reactions.

INTRODUCTION

The catalytic reaction of acetone that has received the most attention is that of hydrogenation. The two possible hydrogenation processes are hydrogen addition across the carbon–oxygen double bond to produce isopropyl alcohol and hydrogenolysis of the hydroxyl group to produce propane. As indicated by Bond (*1*), which of these products predominates, depends upon the catalyst and reaction conditions. Over evaporated films, 2-propanol is the main product with the order of activities being Pt > Ni > Fe = W > Pd > Au (*2*). Deuterium exchange experiments with acetone over evaporated metal films show that the exchange of a single H atom predominates although in some cases, such as Ni, there is substantial multiple exchange (*3*). Bond discusses the mechanisms of the surface reactions in terms of the main surface intermediate being $(CH_3)_2\underset{*}{C}\text{–}OH$, where the * indicates a bond to the surface. On the basis of work reported herein we will propose that a metal–oxygen bond rather than a metal–carbon bond is responsible for bonding most acetone produced complexes to a Ni or Co surface.

Relatively little work has been done which gives data directly interpretable in terms of the surface structures produced by adsorbing acetone. Infrared spectra of acetone adsorbed on porous silica Vycor glass shows a large shift in surface OH bands indicating that the acetone is adsorbed via a hydrogen bond of the acetone oxygen to a surface hydroxyl group (*4*). Similarly acetone adsorbed on silica shows a shift in the surface hydroxyl groups and the C=O stretch of the acetone; again indicating hydrogen bonding of the acetone oxygen to a surface hydroxyl group (*5*). These workers found no infrared evidence of acetone adsorption on silica-supported

Ni and no decomposition of acetone over the silica-supported Ni at 25°C but did not find a slow decomposition to CH_4 and CO at 200°C. Our results are somewhat at variance with these results. Upon exposure of Co and Ni in a hydrocarbon oil to acetone vapor, Blyholder and Neff (*6*, *7*) found no infrared bands for adsorped acetone after evacuation of the cell but on Fe spectra for a species assigned an isopropoxide structure were found (*8*). In reporting (*9*) infrared spectra of species formed from acetone on silica-supported Fe, Co and Ni bands in the 1600–1700 cm^{-1} region were tentatively assigned to acyl structures but the additional work reported here results in modified assignments.

EXPERIMENTAL SECTION

The experimental technique, cells and sample preparation were similar to those used previously (*10*). The KBr infrared windows were sealed to the reaction cell with o-rings. The silica-supported metals were prepared by making a slurry of the hexahydrate of either cobalt or nickel nitrate (J. T. Baker, reagent) with Cab-O-Sil, M5 (G. L. Cabot Co.) so that an ultimate composition of 9% metal and 91% silica was produced. The slurry was dried at 100°C and powdered. Approximately 80 mg of the powder was pressed into a 2.5 cm diameter disk. Reduction of the metal nitrate in the disk was carried out in the infrared cell by a flow of dry, oxygen-free H_2 at 430° for 14 hr. The spectra were recorded over the range 4000–1300 cm^{-1} on a Perkin-Elmer Model 457 spectrophotometer using a pure silica disk in the reference beam. The acetone was purified by evacuation during several freeze–thaw cycles and fractional distillation.

RESULTS

The spectrum of a cell with silica-supported Ni containing 13 Torr of acetone for 11 hr is shown as spectrum A in Fig. 1. The major bands are due to gas phase and physically adsorbed acetone while the weak band at 2145 cm^{-1} is assigned as gas phase CO and part of the 3020 cm^{-1} band may be due to gas phase CH_4 since a spectrum of our gas phase acetone shows no band at 2145 cm^{-1} and the intensity at 3020 cm^{-1} is only 15% of the peak in-

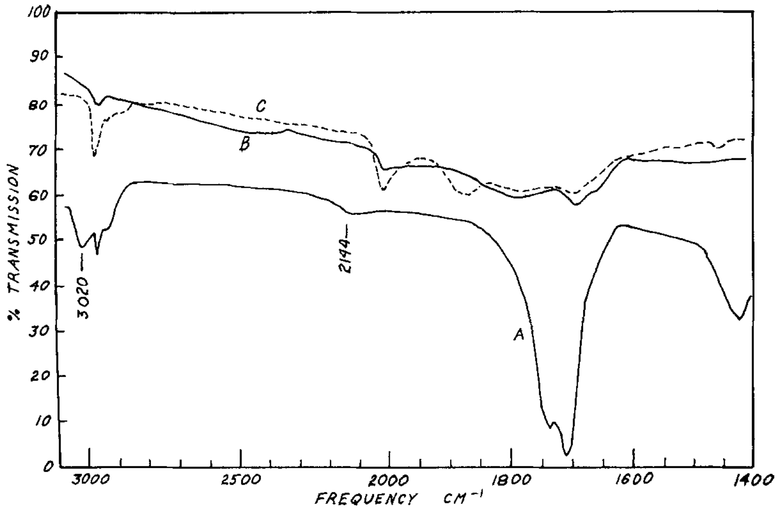

FIG. 1. Acetone at 25°C over silica-supported Ni (previously evacuated at 400°C). (A) gas phase acetone present; (B) cell evacuated for 1.5 hr at 10^{-5} Torr; (C) with H_2 at 60 Torr in cell.

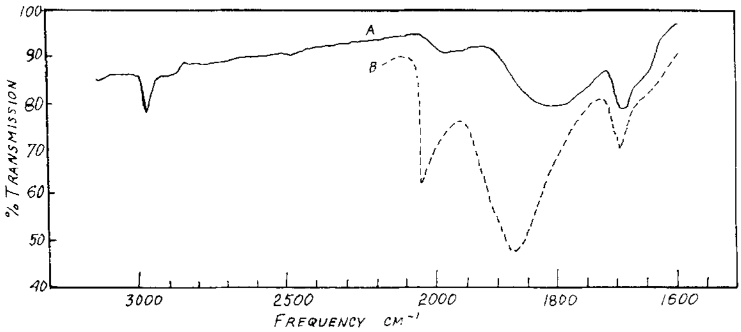

FIG. 2. Acetone at 25°C adsorbed on silica-supported Ni (postreduction cooling in H_2 followed by evacuation at 25°C). (A) cell evacuated for 1 hr after 11 hr exposure to acetone; (B) new sample after (1) CO added and evacuated and (2) acetone added and evacuated.

tensity of the spike at 2975 cm^{-1}. Evacuation of the cell to 10^{-5} Torr for 1.5 hr resulted in spectrum B where the adsorption in the 2050–1750 cm^{-1} region is assigned to chemisorbed CO (*11*) and the small 1700 cm^{-1} band to acetone coordinated via oxygen lone pair electrons to the Ni surface by analogy to acetone adsorbed on silica (*4, 5*) and to acetone complexes (*12*). The very weak band around 2980 cm^{-1} is assigned to the C–H stretch of carbon-hydrogen fragments on the surface. The Ni surface for this sample had been evacuated at 10^{-5} Torr at 400°C just after the reduction procedure and before the adsorption experiments to reduce the amount of residual hydrogen left on the surface to a minimum. Addition of 60 Torr of H_2 to the cell after spectrum B was obtained produced a sample giving spectrum C in Fig. 1. The band which grows in this treatment at 2980 cm^{-1} is assigned to a CH_3 group (*13*) of a surface species. The bands which develop at 2040 and 1880 cm^{-1} in spectrum C are assigned to chemisorbed CO. Since the position of C–O stretching bands for chemisorbed CO in the 1750–2050 cm^{-1} region depend on the exact surface site and the presence of other adsorbed species in ways which are not yet completely understood, the position of the bands in this region are interpreted as having no particular significance beyond indicating the presence of chemisorbed CO.

If the sample is cooled to 25°C from the metal reduction temperature of 400°C in flowing hydrogen before evacuation rather than being evacuated at 400°C as in the case of the previous sample, the infrared spectrum of the surface species produced by exposure to 13 Torr of acetone for 11 hr followed by a 1 hr evacuation at 10^{-5} Torr is shown as spectrum A in Fig. 2. The band assignments are the same as given above. If a similarly prepared fresh sample is exposed at 25°C to 50 Torr of CO for 10.5 hr and evacuated for 4.5 hr, large bands for chemisorbed CO around 2050 and 1900 cm^{-1} are produced. Subsequent exposure of this CO covered surface to 20 Torr of acetone for 9 hr followed by 14 hr of evacuation produced a sample with the spectrum shown as B in Fig. 2. The band assignments are as before.

The spectrum of the surface species remaining after a 3 hr evacuation of a cell which had had 15 Torr of acetone for 10 hr at 90°C over silica-supported Co which had a postreduction evacuation at 400°C is shown as the solid line in Fig. 3. The bands at 2970, 2935, and 2885 cm^{-1} are assigned to CH_3, CH_3 plus CH_2, and CH_2 stretching vibrations, respectively. The bands in the 1430–1470 cm^{-1} region are assigned as CH_3 and CH_2 deformation vibrations. The doublet at 1662 and 1682 cm^{-1} is assigned as the C=O stretch of an acetone molecule coordinated to a surface

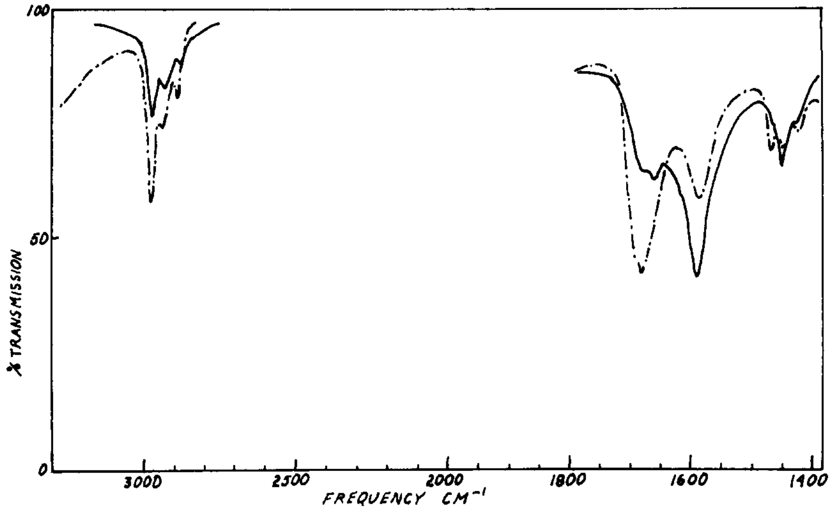

FIG. 3. Acetone adsorbed on silica-supported Co (previously evacuated at 400°C). (——) Sample exposed to 15 Torr of acetone at 90°C for 10 hr and then evacuated; (— ·) spectrum after addition of H_2 at 50 Torr to the cell at 25°C.

metal atom via the lone pair electrons on the oxygen atom in analogy to other acetone complexes (*5*, *12*). The assignment of the band at 1590 cm^{-1} is discussed below. The addition of 50 Torr of hydrogen to the cell at 25°C resulted in the production of the broken line in Fig. 3. Heating the cell with the 50 Torr of hydrogen in it for 2.3 hr at 90°C resulted in spectrum A of Fig. 4 while heating for 14 hr give spectrum B. Evacuation for 15 min produced spectrum C of Fig. 4. The bands in the 1850–2000 cm^{-1} region are assigned to chemisorbed CO.

DISCUSSION

The spectra in Figs. 1 and 2 indicate that some acetone does chemisorb on silica-supported Ni at 25°C in agreement with work done by Blyholder and Wyatt (*9*) and in contrast to the report of Young and Sheppard (*5*) but in view of the large extinction coefficient for the carbonyl stretch the amount of acetone adsorbed

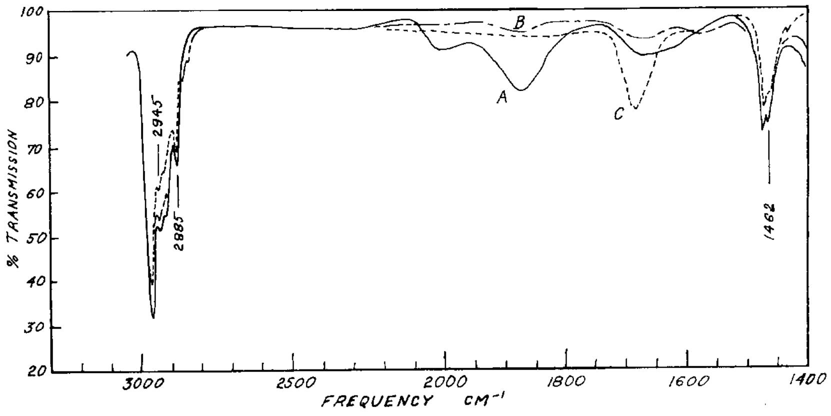

FIG. 4. Acetone on Co. (A) Sample from Fig. 3 after H_2 addition at 50 Torr for 2.3 hr at 90°C; (B) heating continued for 14 hr; (C) sample evacuated.

is small. The small band at 2145 cm^{-1} in curve A of Fig. 1 indicates the formation of gas phase CO from the decomposition of acetone at 25°C on the nickel surface. This is also in contrast to Young and Sheppard's report that they did not observe decomposition until their sample was heated to 200°C. The most probable reason for these differences seems to be the higher reduction temperatures and much longer reduction periods used in this laboratory producing slightly more active Ni surfaces. The Ni surface in spectrum A of Fig. 1 is apparently well covered with decomposition fragments and physically adsorbed acetone since the gas phase CO indicated by the 2145 cm^{-1} band does not produce chemisorbed CO as indicated by the absence of bands in the 2050–1800 cm^{-1} region. Our past experience indicates that this much gas phase CO would produce very large bands for chemisorbed CO on a fresh surface. The growth of the carbon–hydrogen band stretching intensity in the 2800–3000 cm^{-1} region in spectrum C upon hydrogen addition indicates that there were carbon fragments on the Ni surface. Considering the relative intensities of C=O stretching bands and C–H stretching bands in acetone (*5*), the C–H band intensity for the amount of chemisorbed acetone indicated by the intensities of the C=O bands at 1700 cm^{-1} in spectra B and C would be negligible so all of the C-H band intensity is due to surface species other than adsorbed acetone. The band at 1715 cm^{-1} in spectrum A, which is not present in the spectrum of gas phase acetone indicates the presence of adsorbed acetone on the silica support in agreement with Young and Sheppard (*5*) who showed that the acetone on silica pumps off in 1 hr of evacuation. The use of evacuation times greater than 1 hr in our work insures that the bands observed herein are for species adsorbed on the metal and not on the silica support. Removal of some of the surface species by evacuation and hydrogenation in spectra B and C results in some of the surface acetone decomposing to give chemisorbed CO as shown by the appearence of the bands in the 1850–2050 cm^{-1} region.

In Fig. 2 the 1700 cm^{-1} band indicates that acetone will also coordinate with a Ni surface that contains adsorbed hydrogen (spectrum A) or adsorbed CO (spectrum B). The bands between 1750 and 2050 cm^{-1} for chemisorbed CO produced from acetone decomposition in spectrum A indicate that adsorbed hydrogen does not interfere with acetone decomposition, whereas the appearance of only a small band in the C-H stretching region when H_2 is added to the material giving spectrum B indicates that chemisorbed CO does inhibit acetone decomposition.

The intensities of the bands in Fig. 3 being much greater than those in Figs. 1 and 2 indicates that much more acetone adsorbed on the Co surface at 90°C than on the Ni surface at 25°C. The appearance of the doublet at 1662 and 1682 cm^{-1} in the solid line of Fig. 3 is ascribed to acetone adsorbing on two different sites on the Co surface just as CO adsorption on different sites leads to different C–O stretching frequencies (*11*). Comparison of the C–O stretching frequency intensity to the C–H intensities for acetone (*5*) leads to the conclusion that only a small fraction of the C–H intensity in the 2800–3000 cm^{-1} region can be due to adsorbed acetone so there must be considerable amounts of other carbon and hydrogen-containing species on the surface. One likely surface species is an isopropoxide structure like (**II**) in Fig. 5. The relative intensities of the C–H bands in the 2800–3000 cm^{-1} range in Fig. 3 closely resemble those for isopropanol adsorbed on silica-supported cobalt in Fig. 6. This figure is taken from the work of Blyholder and Wyatt (*9*) but only tabular data is given for isopropanol in Ref. (*9*). The idea of the interconversion of coordinated acetone

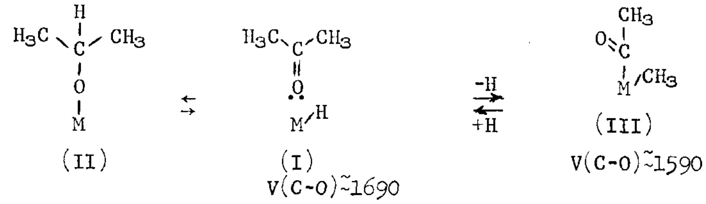

Fig. 5. Structures for chemisorbed acetone.

[structure (I) in Fig. 5] with an isopropoxide structure (II) is further supported by the appearence of the band in Fig. 6 at 1690 cm^{-1} which is assigned as coordinated acetone produced from adsorbing isopropanol. Heating with hydrogen converts most of the surface coordinated acetone to alkoxide as shown by the small intensity at 1690 cm^{-1} in spectra A and B of Fig. 4 while evacuation restores this band in spectrum C as isopropoxide is dehydrogenated to acetone.

It is most likely that there are a variety of structures on the surface since heating the sample with hydrogen results in the large increase in C-H band intensities shown in Fig. 4. The fact that these C–H intensities grow so much upon heating with only hydrogen in the cell indicates that the surface had contained a large number of unsaturated carbon fragments. The relative intensities in Fig. 4 are also somewhat changed from Fig. 3. The C–H intensity pattern in Fig. 4 most closely resembles that of adsorbed *n*-propanol shown in Fig. 7. This again is taken from the work of Blyholder and Wyatt (*9*) which was published in tabular form. Since the C–H intensity patterns would be approximately the same for metal alkyl and metal alkoxide species containing three carbon atoms it is not possible from these spectra to tell the relative quantities of each but we expect both to be present along with species containing lesser and greater numbers of carbon atoms.

Bands around 1590 cm^{-1} as in Fig. 3 have most often been assigned as surface carboxylate groups but, as Fig. 8 shows, a surface carboxylate should have as intense a band around 1420 cm^{-1} as around 1590 cm^{-1} and Fig. 3 is lacking this. The spectrum of the adsorbed acetate group in Fig. 8 is taken from work of Blyholder *et al.* (*14*) which was presented in tabular form. The peak at 1452 cm^{-1} is in the proper location to be assigned as a C–H deformation band and is at a significantly higher frequency than 1420 cm^{-1} where Fig. 8 indicates the symmetric carboxylate stretch is located. It is possible that the small peak at 1430 cm^{-1} should be assigned

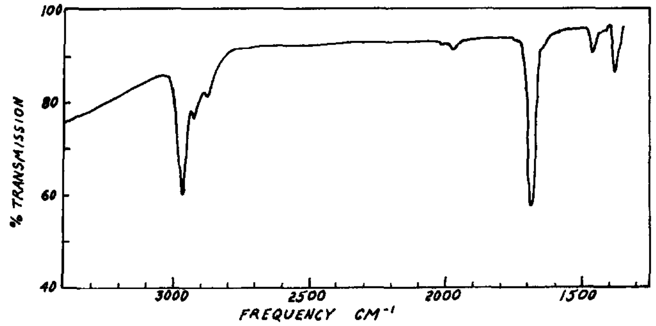

Fig. 6. Isopropanol adsorbed on silica-supported Co; sample evacuated. From the work of Blyholder and Wyatt (*9*).

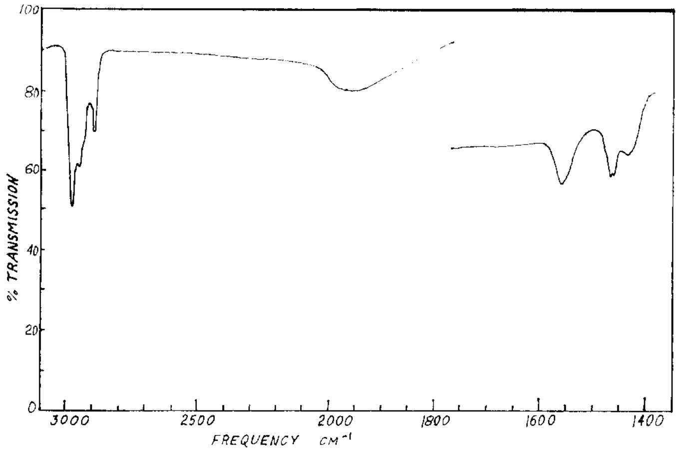

Fig. 7. *N*-Propanol adsorbed on silica-supported Co; sample evacuated.

to a carboxylate structure but even if this is done the relative intensities for the asymmetric and symmetric stretches (*14*) illustrated in Fig. 8 indicate that only a small fraction of the 1590 cm^{-1} band in Fig. 3 should be assigned to a carboxylate structure. Another difficulty with assigning the 1590 cm^{-1} band to a carboxylate is that addition of H_2 at 25°C cuts its intensity in half (Fig. 3) while heating to 90°C (Fig. 4) eliminates it almost completely, whereas it was shown (*14*) that the carboxylate structure is stable on Co up to about 150°C. Also a band at 1460 cm^{-1} remains in Fig. 4 while the 1590 cm^{-1} band is gone; again indicating the independence of these two bands. With a carboxylate structure eliminated, the 1590 cm^{-1} band may be assigned as an acyl structure as shown in (III) of Fig. 5. Acyl Pt, Mn, and Re complexes have been shown (*15–17*) to have C–O stretching bands in the 1560–1640 cm^{-1} region. Addition of acetone to a bare Co surface

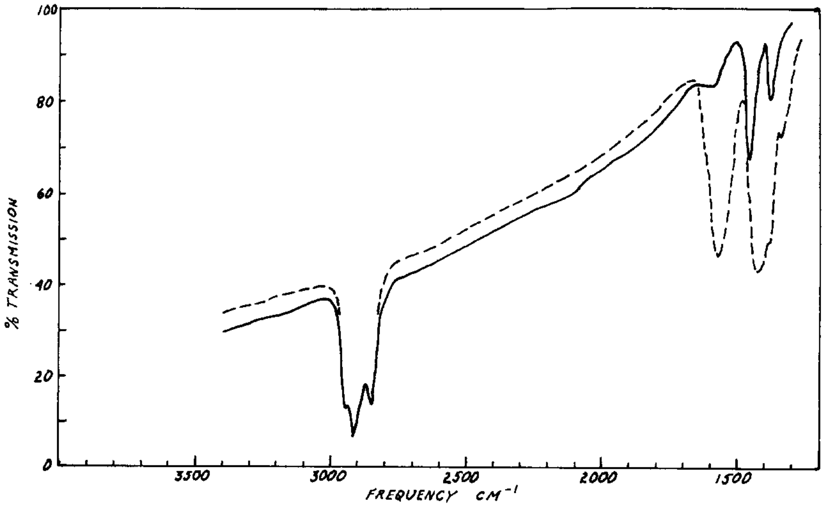

Fig. 8. Acetic acid adsorbed on Fe in an oil matrix. (——) Background. From the work of Blyholder *et al.* (*14*).

resulted in some decomposition of coordinated acetone to an acyl structure as shown in Fig. 5 as evidenced by the 1590 cm^{-1} band in Fig. 3 (solid line). Addition of hydrogen drove the reaction in the reverse direction, i.e., from (III) to (I) in Fig. 5, as shown by the changes in relative intensities of the broken line in Fig. 3. Some of the acyl structure could also be converted to an ethoxide structure by the hydrogen addition. One might expect acyl structures to be readily formed on a Co surface from a primary alcohol where only a C–H bond needs to be broken rather than a C–C bond as in the case of acetone. That this is so is shown by the band at 1590 cm^{-1} in Fig. 9 for ethanol adsorbed on silica-supported cobalt from a spectrum obtained by Blyholder and Wyatt (*9*) which was only reported in tabular form. The band at 1460 cm^{-1} in Fig. 9 is assigned to CH_3 and CH_2 deformation vibrations because this is the correct location for such vibrations and a band at this frequency occurs (*9*) for ethanol adsorbed on silica-supported Fe where only an alkoxide structure is produced and the 1590 cm^{-1} band is absent. This evidence of the independence of the 1590 and 1460 cm^{-1} bands supports the assignment of the 1590 cm^{-1} band to an acyl structure rather than assigning both to a carboyxlate structure. Also the 1590 cm^{-1} band has the wrong shape to be assigned to a carboxylate structure since it is narrow and sharp, whereas the carboxylate bands in Fig. 8 are broad with rounded tops.

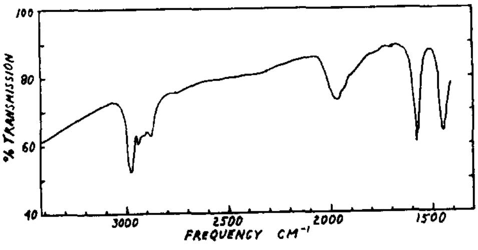

FIG. 9. Ethanol adsorbed on silica-supported Co; sample evacuated. From the work of Blyholder and Wyatt (*9*).

Although Bond (*1*) discussed reactions of acetone on metal surfaces in terms of the structure $(CH_3)_2\underset{*}{C}{-}OH$ we find no infrared evidence for this structure, in particular we never observe a free O–H stretch for a metal surface species. Carboxylate structures with metal–oxygen bonds have been found to be quite stable on Fe, Co and Ni (*14*). Alkoxide structures are very stable on V, Cr, Mn and Fe, while on Ni decomposition to chemisorbed CO and alkyl fragments occurs readily (6–9). On cobalt a mixture of structures like those shown in Fig. 5 are obtained.

In summary it has been shown that acetone does chemisorb on silica-supported Ni at 25°C but the amount is small. The structure of the adsorbed species is that of acetone coordinated through the oxygen atom. There is also some decomposition to CO and hydrocarbons at 25°C. On cobalt much more acetone adsorbs at 90°C with isopropoxide, coordinated acetone, and acyl groups as the initial surface structures.

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