

Infrared Spectra of Hydrocarbons Chemisorbed on Silica-Supported Metals

I. Experimental and Interpretational Methods; Acetylene on Nickel and Platinum

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A description is given of the experimental methods and spectroscopic interpretational procedures used in a series of studies of the infrared spectra of hydrocarbons chemisorbed on silica (pressed Cab-O-Sil disc) supported metals.

Infrared spectra have been obtained from the surface species formed by initial adsorption, and subsequent hydrogenation, of acetylene on silica-supported nickel and platinum.

On nickel, absorption bands from $=CH-$, CH_2 , and CH_3 groups are obtained on initial adsorption. The former probably correspond to $MCH=CHM$ surface species ($M = \text{metal}$), and the latter to surface alkyl groups formed by self-hydrogenation and polymerization processes. After hydrogenation the spectra indicate the presence of surface attached n -butyl groups, $M(CH_2)_nCH_3$. ($n = 3$.)

On platinum a weak initial spectrum is obtained and a large intensity increase occurs on hydrogenation. This indicates that the dissociation of acetylene to form a surface carbide together with MH bonds is greater on platinum than on nickel. The surface species after hydrogenation are alkyl groups with an average value of $n \geq 4$. i.e. the degree of surface polymerization is somewhat greater on platinum. The published spectra from acetylene on palladium and copper are similar to those on platinum except that the initially adsorbed species have a higher proportion of olefinic CH bonds.

It is suggested that the relatively smaller activity of nickel as compared with platinum for the acetylene hydrogenation reaction is related to a higher proportion of hydrocarbon surface residues (and a smaller proportion of MH bonds) formed by adsorption on nickel.

1. INTRODUCTION

In this first paper of a series on the infrared spectra of hydrocarbons adsorbed on silica-supported metals, we deal with experimental methods and spectroscopic interpretational procedures. We also describe and discuss the spectra obtained from acetylene chemisorbed on pressed

discs of Cab-O-Sil supported nickel and platinum.

Infrared spectra from acetylene adsorbed on silica-supported metals have been described previously. Eischens and Pliskin (1, 2) studied "bare" and "hydrogen-covered" nickel supported on powdered Cab-O-Sil. Little, Sheppard, and Yates (3) studied acetylene adsorbed on porous-glass supported copper, nickel and palladium, although their spectra on nickel suffered from very poor transmission. Clark and Sheppard (4, 5) obtained spectra on porous-glass supported palladium and platinum. Dunken, Schmidt, and

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Hobert (6) studied the surface species involved in the hydrogenation of acetylene over silica and magnesia supported palladium. Nash and De Sieno (7) have also reported spectra from acetylene adsorbed on fine copper, nickel or palladium particles formed by exploding metal wires.

Because different workers have used different metals or supports, or both, and there is the possibility of complications caused by minor nonsilica constituents in porous glass (7), it seemed worthwhile to re-study the infrared spectra of chemisorbed acetylene on nickel and platinum using pressed Cab-O-Sil/metal discs. The higher performance obtainable from a diffraction grating infrared spectrometer also enables better quality spectra to be obtained than previously. The conclusions of the earlier studies are discussed below in relation to the present results.

2. EXPERIMENTAL

Samples of nickel supported on Cab-O-Sil were prepared by impregnating Cab-O-Sil H5 with a solution of nickel nitrate (reagent grade). The mixture was stirred until a creamy paste was formed and dried overnight at 110°C. The samples contained 10% of nickel. The Cab-O-Sil supported nickel nitrate was finely ground in a mortar and 0.1 g portions pressed in a 1-in diameter die at a pressure of 3-4000 lbs in⁻². The sample weight was 20 mg cm⁻². Cab-O-Sil supported platinum samples containing 10% of metal were prepared in a similar manner using solutions of platinum chloride.

The infrared cell used was similar to that described by Little, Sheppard, and Yates (3) except that the silica/metal disc slid between the furnace and infrared window parts of the cell in a glass framework. It was attachable to a conventional vacuum system capable of achieving a vacuum of 10⁻⁶ Torr. Spectra were recorded on a Grubb-Parsons GS 2 spectrometer with a resolution of about 3 cm⁻¹.

After insertion in the cell, the samples were evacuated at room temperature, and then at gradually increasing temperatures up to 130°C, until a vacuum of 10⁻³ Torr was obtained. Hydrogen was then admitted to the cell and the temperature gradually increased over 1 hr to 350°C. The sample was then maintained at 350°C for 16 hr in hydrogen. "Bare" metal samples were produced by evacuating the sample for one hour at 350°C. "Hydrogen covered" samples were produced by cooling the sample to room temperature followed by evacuation for 30 sec. Typical nickel samples transmitted 25-40% of the incident radiation, and the platinum samples 45-50%, at 3000 cm⁻¹. A transmission spectrum through a typical silica/platinum disc is shown in Fig. 1.

The acetylene used in the experiments described here was obtained from the Chemical Research Laboratory, Teddington and was of 99.98% purity. Apart from degassing by the freeze-pump-thaw technique, it was used without further purification.

Acetylene was admitted to the metal/silica sample at 10 Torr and about one

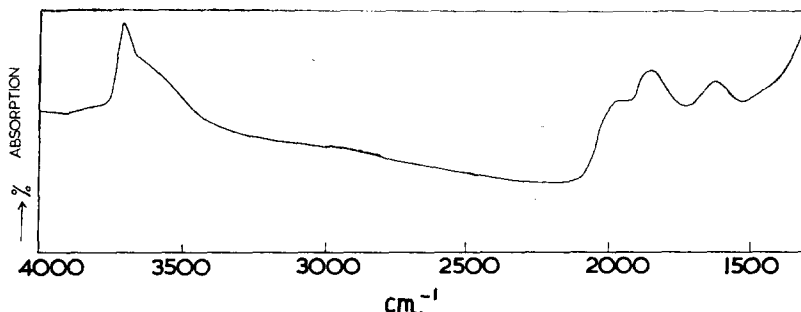


FIG. 1. The transmission spectrum through a typical platinum/silica disc in the range 4000 to 1300 cm⁻¹, obtained on a double-beam spectrometer without attenuation of the reference beam.

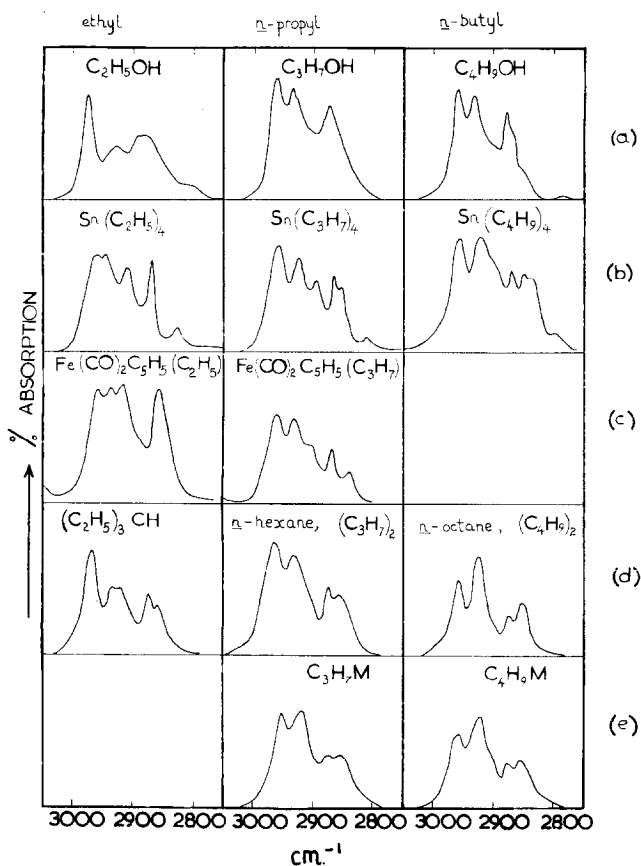


FIG. 2. Infrared spectra in the CH bond stretching region ($3050\text{--}2750\text{ cm}^{-1}$) for ethyl, *n*-propyl, and *n*-butyl groups attached (a) to oxygen atoms in ethanol, *n*-propanol and *n*-butanol, (b) to tin atoms in tin-tetraethyl, tin tetrapropyl and tin tetrabutyl, (c) to iron atoms in $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{R}$ ($\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$), (d) to carbon atoms in 3-ethyl pentane (Et_3CH), *n*-hexane (di-*n*-propyl) and *n*-octane (di-*n*-butyl) [(a) to (d) all in CCl_4 solution] and (e) attached to surface nickel atoms as surface hydrogenation products from the chemisorption of propene and 1-butene.

hour later the spectra of the gas phase and the gas phase plus adsorbed species were recorded. The system was allowed to stand overnight and the two spectra were recorded again the next morning. The gaseous and physically adsorbed acetylene was removed by evacuation, first for 30 sec (this time was found to be sufficient to remove this hydrocarbon from Cab-O-Sil), and then for 30 min, and the spectrum of the species remaining adsorbed on the surface was recorded. The sample was again evacuated and the spectrum recorded until

no further changes in the spectrum were observed.

Hydrogen (300 Torr) was admitted to the sample and the spectra of the gas, and gas plus adsorbed phase, were observed both after 1 hr and overnight standing. Spectra of the species remaining after pumping for a few seconds, and after pumping for longer times, were obtained; also those obtained after readmitting hydrogen to the sample were recorded.

All spectroscopic experiments described in this paper were carried out at ambient

temperature ($\sim 20^\circ\text{C}$). The metal/silica sample was probably at somewhat higher temperature when in the infrared beam due to absorption of radiation. The extent of this temperature rise will be variable, but greater in the absence of a gas phase.

The alcohols, tin tetraalkyls, and hydrocarbon model compounds whose spectra are shown in Fig. 2 were obtained from commercial sources and purified by distillation if not already of high purity. The spectra of compounds of formulae $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)\text{R}$, [$\text{R} = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$] were donated to us by Dr. M. H. L. Green, now of Oxford University. We are very grateful to Dr. Green for these spectra.

3. INTERPRETATION OF SPECTRA OF CHEMISORBED HYDROCARBONS

The interpretation of the spectra of chemisorbed species must of necessity be carried out by reference to the spectra of

model compounds of known structure (1). However many spectra of hydrocarbons have been analyzed in detail (9), and the conclusions—particularly with respect to intensities—have been recently reviewed by Wexler (10). Infrared data of model metal-hydrocarbon groupings are more scattered in the literature (11), but we have attempted to assess the situation in the 3000 cm^{-1} (νCH) region with respect to alkyl groups attached to tin and iron atoms in some model compounds. Spectra of ethyl, *n*-propyl and *n*-butyl groups attached to one or both of these metals are shown in Figs. 2c and 2d.

Following procedures deployed first by Eischens and Pliskin (1), three types of data have been used to analyze the spectra of chemisorbed hydrocarbon groupings. These are (1) the frequencies of the infrared bands; (2) the ratio of optical densities (peak intensities) of the antisymmetrical νCH_3 and νCH_2 group absorptions

TABLE 1
INFRARED FREQUENCY AND INTENSITY DATA FOR HYDROCARBON GROUPINGS

| Group | Frequencies (9, 10) | Assignments (9) | Peak intensities per group (10, 14) (apparent molecular extinction coefficient) | Integrated intensities per group (10) (practical units) |
|---------------------------|---|---|--|---|
| $\text{C}\equiv\text{CH}$ | 3300-3250 ^a | νCH | | 0.3-0.85 ^a |
| $\text{C}-\text{CH}_2$ | $\left\{ \begin{array}{l} 3080 \pm 10 \\ \sim 2980 \end{array} \right.$ | $\left\{ \begin{array}{l} \nu\text{CH}_2 \text{ as.} \\ \nu\text{CH}_2 \text{ s.} \end{array} \right.$ | $\sim 19.0^b$ — | 0.10 — |
| $\text{C}=\text{CH}$ | 3025 ± 10 | νCH | $\sim 14.6^b$ | 0.075 ± 0.025^c |
| CH_3-C | $\left\{ \begin{array}{l} 2955 \pm 5 \\ 2870 \pm 5 \\ 1462 \pm 5 \\ 1380 \end{array} \right.$ | $\left\{ \begin{array}{l} \nu\text{CH}_3 \text{ as.} \\ \nu\text{CH}_3 \text{ s.} \\ \delta\text{CH}_3 \text{ as.} \\ \delta\text{CH}_3 \text{ s.} \end{array} \right.$ | $\left\{ \begin{array}{l} 129 \\ 55 \\ 17.5 \\ 20.5 \end{array} \right.$ | $\left\{ \begin{array}{l} \\ \\ \\ 0.048 \end{array} \right.$ |
| | $\left\{ \begin{array}{l} 2927 \pm 5 \\ 2855 \pm 5 \end{array} \right.$ | $\left\{ \begin{array}{l} \nu\text{CH}_2 \text{ as.} \\ \nu\text{CH}_2 \text{ s.} \end{array} \right.$ | $\left\{ \begin{array}{l} 77 \\ 46 \end{array} \right.$ | $\left\{ \begin{array}{l} \\ \\ \sim 0.03 \\ \sim 0.35 \end{array} \right.$ |
| | ~ 1467 | δCH_2 | 8 | 0.02 |
| | ~ 2890 | νCH | — | ~ 0.14 |

^a The lower frequencies and higher intensities for $\text{C}\equiv\text{CH}$ are caused by hydrogen bonding.

^b Values estimated by Ward (12, 15) relative to the νCH_2 (as.) band.

^c Comparison of Refs. (17) and (10) indicates that the values given for *trans* and *cis* in Ref. 10, Table 5 corresponds to two $=\text{CH}$ groups.

near 2955 and 2925 cm^{-1} respectively, together with—when applicable—the ratio of the =CH- and CH_2 absorptions near 3025 and 2925 cm^{-1} ; and (3) the ratio of the total integrated intensities in the νCH region before and after hydrogenation (total intensities are measured in order to overcome difficulties caused by multiple overlapping bands).

The frequencies, assignments, and intensity data for the main types of groupings in hydrocarbons themselves (9, 10) are summarized in Table 1. It is to be expected that the general frequency ranges for CH bonds attached to sp , sp^2 , and sp^3 hybridized carbon atoms (3300–3250; 3100–2980; and 3000–2750 cm^{-1} , respectively) will be retained with little modification for groups attached to the metal surface.

The spectra of model compounds with $\text{CH}_3\text{-M}$ groups suggest that the $\nu\text{CH}_3(\text{as.})$ and $\nu\text{CH}_3(\text{s.})$ bands are usually somewhat raised in frequency relative to $\text{CH}_3\text{-C}$ groups (Table 2A). In addition to the two strong fundamentals most of these spectra show a band of appreciable intensity in the region 2830–2800 cm^{-1} which is not found in the spectra of hydrocarbons. This band is likely to represent the overtone of the $\delta\text{CH}_3(\text{as.})$ fundamentals of $\text{CH}_3\text{-M}$ groups (which occur in the region 1430–

1400 cm^{-1}) (12), the overtone being probably in Fermi resonance with the $\nu\text{CH}_3(\text{s.})$ fundamental and hence raised in intensity.

CH_2M groups probably show similar changes in their νCH fundamental frequencies but overlapping bands from the remainder of the alkyl chains partially obscure this region. The spectra illustrated in Fig. 2 consistently show prominent bands in the 2920–2895 cm^{-1} region and weaker ones between 2835 and 2815 cm^{-1} which can be attributed to $\text{-CH}_2\text{M}$ groups. The former represents either a lowered $\nu\text{CH}_2(\text{as.})$ (11) or a raised $\nu\text{CH}_2(\text{s.})$ fundamental compared with the hydrocarbons (the latter seems rather more probable because of the regularities described above in the spectra of $\text{CH}_3\text{-M}$ compounds with the same metal atoms) and the latter is probably the δCH_2 overtone band. By analogy with hydrocarbon spectra, somewhat abnormal group frequencies (usually higher in value) may be found if the $\text{-CH}_2\text{M}$ group etc. is part of a small strained ring (9).

Figure 2 also enables spectra of surface species obtained by hydrogenation of C_3 and C_4 olefins chemisorbed to silica-supported metal (12) (predominantly n -propyl or n -butyl groups), to be compared with those from model compounds.

TABLE 2

| A. Observed frequencies of $\text{CH}_3\text{-M}$ groups in the 3000 cm^{-1} (νCH) region | | |
|---|---|---|
| Group | Observed frequencies | Compound |
| $\text{CH}_3\text{-C}$ | $\sim 2960(\text{s})$ $\sim 2875(\text{m})$ | Hydrocarbons |
| $\text{CH}_3\text{-Sn}$ | 2979(s), 2915(s), | $(\text{CH}_3)_4\text{Sn}^a$ |
| $\text{CH}_3\text{-Pb}$ | 2999(s), 2915(s), | $(\text{CH}_3)_4\text{Pb}^a$ |
| $\text{CH}_3\text{-Fe}$ | 2971(s), 2897(s), 2815(mw) | $\text{CH}_3\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)^b$ |
| $\text{CH}_3\text{-Pd}$ | 2944(s), 2875(s), 2790(vw) | $(\text{CH}_3)_2\text{Pd}(\text{Ph}_3\text{P})_2^c$ |
| $\text{CH}_3\text{-Pt}$ | $\sim 2930(\text{m})$, 2885(m), 2815(m) | <i>trans</i> $\text{CH}_3\text{Pt Cl}(\text{PMe}_3)_2$ |
| | $\sim 2930(\text{m})$, 2872(m), 2803(m) | <i>cis</i> $(\text{CH}_3)_2\text{Pt}(\text{PMe}_3)_2$ |
| B. Peak intensity (extinction coefficient) ratios for hydrocarbon groupings | | |
| (a) Observed 2925/2955 ratio for $\text{CH}_3(\text{CH}_2)_n^{14}$ | | |
| ~ 0.7 ($n = 1$); 1.0 ($n = 2$); 1.4 ($n = 3$); 1.8 ($n = 4$); 2.1 ($n = 5$). | | |
| (b) Approximate 3025/2925 ratio for $\text{=CH-}/\text{CH}_2$ groups (12, 15) = 0.19 ± 0.03 . | | |
| (c) Approximate 3080/3025 ratio for $\text{=CH}_2/\text{CH}_2$ groups (12, 15) = 1.3 ± 0.1 . | | |

^a Young, Koehler, and McKinney, *J. Am. Chem. Soc.* **69**, 1410 (1947).

^b Supplied by Dr. M. H. L. Green.

^c Spectral data supplied by Prof. G. E. Coates.

The spectra of the chemisorbed species appear to fall somewhere between those of the hydrocarbons and the metal-alkyl compounds. Significantly they differ markedly from those of the alkyl-O compounds (Fig. 2a). This shows that the chemisorbed species are not attached to the silica surface of the adsorbent, as a result of a metal-catalyzed reaction of the hydrocarbon with surface SiOH groups. Spectra of such secondary products have been found in studies of the chemisorption of more polar molecules, such as aldehydes and ketones, on metal/silica samples (13).

By detailed analysis of the νCH spectra of a series of *n*-alkanes (14), it has been shown that the νCH_3 (as.) band near 2955 cm^{-1} remains of approximately constant peak intensity (when expressed in optical density), whereas the νCH_2 (as.) band near 2925 cm^{-1} increases linearly in optical density with the number of CH_2 groups. The $2925/2955\text{ cm}^{-1}$ peak intensity ratio is therefore a useful measure of alkyl chain-length. The rounded-off *observed* values for this ratio for the alkanes are listed in Table 2B. These differ slightly from ratios calculated from the intensities of individual groups as given in Table 1, because of the overlap of the νCH_3 band by the tail of the νCH_2 band. Linear alkenes give somewhat lower values of the $2955/2925$ intensity ratio (15) because of a weaker intensity from CH_2 groups adjacent to double bonds (10, 12, 15). When the hydrocarbon-derived intensity ratios are used to analyze the composition of surface alkyl groups, uncertainties arise because of changes in intensity or position of the νCH_2 (as.) band from $-\text{CH}_2\text{M}$ groups. The appearance of spectra of model metal-alkyl compounds (Fig. 2) and rough measurements of integrated νCH intensities (5) suggest that CH bonds attached to metal atoms do not differ greatly in intensity ($\pm 50\%$) from those attached to carbon. Shifts in position of $-\text{CH}_2\text{M}$ bands will lead to observed $2925/2955$ intensity ratios that are smaller than those observed in hydrocarbons i.e. use of the hydrocarbon data is likely to lead to an underestimate (by not more than one

methylene unit) of the ratio of CH_2 to CH_3 groups. The shifted $-\text{CH}_2\text{M}$ band in the region of $2920\text{--}2895\text{ cm}^{-1}$ may be a contributing factor in the observation that the spectra of surface-attached alkyl groups seem to have a less pronounced minimum between the νCH (as.) and νCH (s.) absorption regions in comparison with the hydrocarbons (Fig. 2). Also changes in νCH_2 (s.) frequencies of metal-attached groups can lead to a change in pattern of absorption in the $2870/2855\text{ cm}^{-1}$ region, with the methyl band near 2870 cm^{-1} relatively somewhat stronger than in spectra from the same *n*-alkyl groups in model hydrocarbons.

Values have not been given in the literature for the ratio of peak intensities of $=\text{CH}-$ and CH_2- bands near 3025 and 2925 cm^{-1} , respectively. From analysis of published spectral data and new experimental data Ward (12, 15) has estimated the $3025/2925$ ratio to be 0.1 *q* for equal numbers of such *groups* (not CH bonds).

The third method used to interpret the spectra of adsorbed hydrocarbon groupings involves the use of total *integrated* intensities (from extinction coefficient *v.* cm^{-1} curves) in the νCH region ($3100\text{--}2750\text{ cm}^{-1}$) before and after hydrogenation. Mean values for the molar intensities of CH_3 , CH_2 , and CH groups in hydrocarbons differ somewhat in the literature (10, 16, 17), but the value does not appear to differ greatly *per CH bond* for the several types of sp^3 hybridized groupings whose absorption bands occur in the $3000\text{--}2800\text{ cm}^{-1}$ region. On the other hand the *integrated* intensity per sp^2 hybridized $=\text{CH}-$ bond (3025 cm^{-1} region) is less by a factor of two to three in hydrocarbon spectra (1, 10, 16). It has been mentioned above that measurements on model compounds do not suggest that any considerable change in *integrated* intensity occurs for >CH-M groups as compared with >CH-C . On the other hand, infrared intensities are rather sensitive to structural change, and experimental errors arise in connection with the necessity of separately assessing the in-

egrated intensities of surface and gas phase species after hydrogenation.

However, as will be encountered below in our experimental results with chemisorbed acetylenes, large values of integrated intensity ratios (after hydrogenation)/(before hydrogenation) are often observed. Despite quantitative uncertainties, these undoubtedly give useful qualitative information about the general extent to which dissociative initial adsorption occurs, whereby C-H bonds are replaced by M-H bonds. Also, because the identity of the surface and gas-phase species can often be determined after hydrogenation, hypotheses about the nature of the initial species can often be checked by use of the intensity ratio.

As can be seen from Table 1, the intensities of ν CH modes are much stronger than those of the δ CH type. Furthermore the latter occur in a region of strong silica background absorption. Nevertheless in favorable cases data from this lower frequency region are of considerable value also.

4. RESULTS

4.1. Hydrogen-Covered Nickel

When acetylene was left in contact overnight with pressed discs from Cab-O-Sil supported nickel the infrared spectrum gave the bands in the ν CH region with the frequencies listed on the top line of Table 3. Additional bands occurred at 3315 cm^{-1} and 3266 cm^{-1} (gaseous and physically adsorbed acetylene) which disappeared after pumping for 30 sec. The resulting spectrum remained unaltered by further pumping for 30 min and is shown in Fig. 3(a). Only acetylene was observed in the gas phase before pumping. No bands were observed in the ν C \equiv C and ν C=C or CH angle-bending regions between 2300 and 1300 cm^{-1} .

Analogous data are also recorded in Table 3 for the spectrum obtained after hydrogenation with an excess of gas-phase hydrogen (Fig. 3b). In this case a weak band also occurred in the 1450 cm^{-1} region but, either before or after hydrogenation, our spectra all appear to be con-

TABLE 3
FREQUENCY AND INTENSITY DATA FOR SURFACE SPECIES PRESENT AFTER INITIAL ADSORPTION
AND HYDROGENATION OF ACETYLENE ON SILICA-SUPPORTED METALS

| | Frequencies observed | Total integrated area | Area ratio | Intensity ratio ^a 2925/ 2955 ^b | Intensity ratio ^a 3020/ 2925 | Approx. surface composition =CH/CH ₂ / CH ₃ |
|-----------------------|-------------------------------|-----------------------------|--------------------|---|--|---|
| "Hydrogen-covered" Ni | | | | | | |
| Initial adsorption | 3025, 2965, 2930, 2875, | 457 | | ~ 1.0 ^f | 0.19 | 1.0/2.0/1 |
| Hydrogenation | 2950, 2925, 2875 (1450) | 744 ^c | (1.6) ^e | 1.2 | 0.0 | -/ \sim 2.5/1 |
| "Bare" Ni | | | | | | |
| Initial adsorption | 3020, 2967, 2937, 2875, | 421 | | ~ 1.0 ^f | 0.40 | 2.1/2.0/1 |
| Hydrogenation | 2957, 2925, 2875 | 725 | (1.7) ^e | 1.25 | 0.0 | -/ \sim 2.6/1 |
| "Hydrogen-covered" Pt | | | | | | |
| Initial adsorption | 3018, 2962, 2925, 2875, 2850, | 95 ^d | | ~ 1.6 | ~ 0.2 | |
| Hydrogenation | 2953, 2917, 2873, 2854 | 716 | (7.5) | 1.6 | 0.0 | -/ \sim 4/1 |

^a Ratios of peak optical densities.

^b The actual frequencies observed for the peaks vary from spectrum to spectrum as specified.

^c 669 after pumping for 30 secs.

^d After pumping for 30 minutes.

^e Intensity ratio (After hydrogenation/before hydrogenation).

^f After approximate allowance for overlapping absorption (see text).

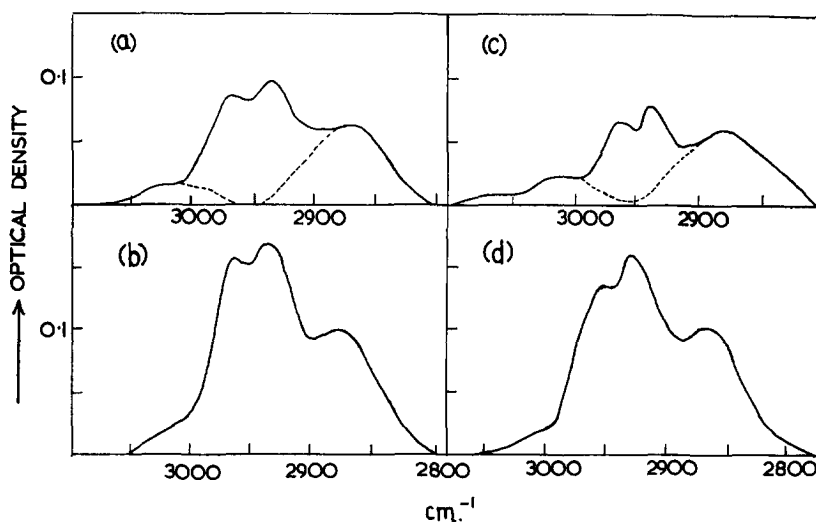


FIG. 3. Acetylene chemisorbed on silica-supported nickel (a) initial adsorption on hydrogen covered nickel followed by evacuation after 30 min, (b) after hydrogenation, (c) initial adsorption and evacuation on 'bare' nickel, (d) hydrogenation of (c). The dotted lines indicate the assumed "background" when estimating the 2925/2955 intensity ratio (Table 3).

siderably weaker in the angle deformation region ($1500\text{--}1350\text{ cm}^{-1}$) relative to the νCH region than those observed by Eischens and Pliskin (1). No measurable bands appeared in the gas phase. Table 3 also gives information about the total intensity of absorption in the $3100\text{--}2750\text{ cm}^{-1}$ region before and after hydrogenation, and on the ratios of the peak-heights (in optical densities) of the 2925/2955 and 3025/2925 pairs of absorption bands, which are of structural significance (see above). Pumping out the gas phase for 30 sec from the hydrogenated sample led to only a slight decrease in the total intensity of the spectrum (by 10%). No further changes occurred on pumping for a further 30 min.

4.2. "Hydrogen-Free" Nickel

Rather similar spectra were obtained when the above sequence of experiments was repeated with "hydrogen-free" nickel. The spectra obtained are shown in Figs. 3(c) and 3(d), and the relevant numerical data are also listed in Table 3. The main differences between the spectra from "hydrogen-covered" and "bare" samples are, (1) a stronger band near 3020 cm^{-1} from initial adsorption on the "bare" sample, (2)

a different intensity distribution in the $2900\text{--}2800\text{ cm}^{-1}$ region on initial adsorption (compare Figs. 3a and 3c) and (3) a somewhat greater intensity enhancement on hydrogenation of the spectrum on bare nickel leading, however, to a very similar hydrogenated intensity (Table 3).

4.3. The Hydrogenation of Acetylene over Nickel

Addition of premixed acetylene and hydrogen (1:1) to a "bare" catalyst resulted in no detectable formation of ethylene or ethane, even after addition of more hydrogen to give an acetylene to hydrogen ratio of 1:50. Addition of a similar mixture to a "hydrogen-covered" catalyst resulted in the production of a mixture of ethane and ethylene. No polymerization products were detected in the gas phase, although the sensitivity of the infrared method for detecting these is not high.

4.4. "Hydrogen-Covered" Platinum

Only acetylene was observed in the gas phase after standing in contact with a hydrogen-covered platinum sample. Bands due to gas phase and physically adsorbed acetylene were removed by 30 sec pumping; a further 30 min evacuation led to only a

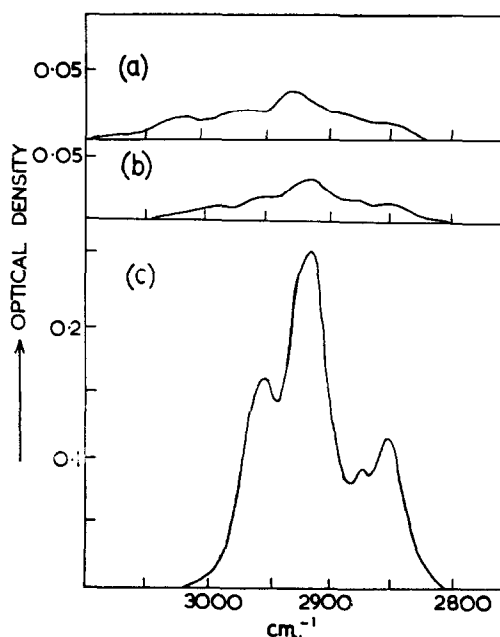


FIG. 4. Acetylene chemisorbed on hydrogen covered platinum (a) initial adsorption followed by evacuation for 30 sec, (b) evacuation for 30 min and (c) after overnight hydrogenation.

slight further intensity decrease. The relevant frequency and intensity data, before and after hydrogenation, are also given in Table 3, and the spectra are illustrated in Fig. 4. Evacuation of the gas phase from the hydrogenated sample for 30 sec led to a decrease in band area from 716 to 503 units, and for 30 min to 283 units; re-addition of hydrogen restored the intensity to 781. The two steps of evacuation were also accompanied by changes in the 2917/2953 peak intensity ratio from 1.6 to 1.35 and 1.25, respectively; rehydrogenation gave the original value of 1.6 again.

5. INTERPRETATION OF SPECTRA

5.1. Adsorption on Nickel Surfaces

5.1.1. Spectra obtained after hydrogenation. These (Figs. 3a and 3c) were closely similar whether the original surface was "hydrogen-covered" or "bare" except for a small change in the 2925/2955 cm^{-1} ratio. All the absorption bands occur in the region characteristic of saturated hydrocarbon groupings; the 2925/2955 ratio, as

well as the general appearance of the spectra, suggests that the mean composition approximates to that of a *n*-butyl group (see Section 3). This conclusion is in close agreement with that reached earlier by Eischens and Pliskin (1) and indicates a limited degree of polymerization on the surface. We shall comment below on the increase in intensity on hydrogenation.

5.1.2. The spectra of the initially adsorbed species. These are perhaps of greater interest. Our results differ from those reported by Eischens and Pliskin (1, 2) and by Nash and De Sieno (7) in that we have observed bands attributable to $=\text{CH}-$ groups near 3020 cm^{-1} in both cases whereas they did not do so. However these are the weakest bands in the spectra, and Eischens and Pliskin's measurements were made using a prism spectrometer with considerably lower resolution and sensitivity. The difference may therefore be more apparent than real.

The adsorption literature provides clear evidence that acetylene is very strongly chemisorbed on transition metals (18, 19). The slow rate of the hydrogenation reaction that occurs if the metal is first exposed to the hydrocarbon is caused by the virtually complete coverage of the surface by hydrocarbon residues leading to zero or negative orders of reaction with respect to acetylene (20). Our finding that the hydrogenation of acetylene only occurs to a considerable extent when the acetylene/ H_2 mixture is introduced to "hydrogen-covered" nickel (Section 4.3) is consistent with this viewpoint.

Sheridan (18) and Bond (19) postulate that the adsorption of acetylene on this metal leads to surface $\text{MCH}=\text{CHM}$ groups. The absorption bands found in the infrared spectra near 3020 cm^{-1} are very probably attributable to this type of surface species although a polymerized species of type $\text{MCH}=\text{CH}-\text{CH}=\text{CHM}$ would give a closely similar spectrum. In common with Eischens and Pliskin (1), we can conclude with some confidence from the infrared spectra that a major fraction of the initial surface species have CH bonds attached to sp^3 hybridized carbon atoms

(Table 3). Eischens and Pliskin suggest that these correspond to a surface ethyl group. The 2925/2955 optical density ratio of the CH₂ and CH₃ groups in our spectra from the initial species suggests the presence of on average about 2.0 CH₂ groups per CH₃ group, although there is some uncertainty because of the additional overlapping absorption at the lower frequency. This result is most readily interpreted in terms of a mixture of surface ethyl and *n*-butyl groups (assuming that species with even numbers of carbon atoms are likely) with the latter predominating.

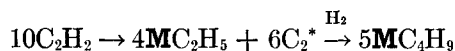
As some saturated alkyl bands are readily observed after adsorption, even on nominally "bare" nickel, they are probably formed by self-hydrogenation of acetylene on the metal surface as postulated by Douglas and Rabinovitch (21) from analysis of gas-phase products.

The somewhat greater strength of both the 2955 and 2925 cm⁻¹ bands found on initial adsorption on "hydrogen-covered" nickel (Table 3) is consistent with additional hydrogenation resulting from the hydrogen atoms originally covering the surface, partially at the expense of olefinic surface species (weaker 3020 cm⁻¹). The additional background intensity found in the 2920–2840 cm⁻¹ region (particularly evident in the weaker spectrum on "bare" nickel, but probably also present to a comparable extent in the spectrum on "hydrogen-covered" nickel) may correspond to the presence of saturated surface species of the type M₂CH-, MCH₂-, or -CHM-, which are thought to contribute to a broadish band near 2890 cm⁻¹ in the infrared spectrum obtained from the adsorption of ethylene on nickel (22).

5.1.3. Intensity increase on hydrogenation. We have seen in Section 3 that the increase in integrated intensity in the νCH region on hydrogenation, and particularly the ratio of intensity after hydrogenation to that before, is also of relevance in considering the nature of the surface species. The fact that this increase (Table 3) is somewhat greater from hydrogenation of the "bare" relative to the "hydrogen covered" surface is qualitatively as ex-

pected; the close coincidence of the final intensities in the two spectra indicate that the latter species are very similar.

The self-hydrogenation process discussed in the Section 5.1.2. must be accompanied by the production of a compensating proportion of hydrogen-deficient species, probably of the "surface carbide" type (1). These, although not observable in the initial spectra, will contribute to the hydrogenation intensity change. For example, assuming equal intensity contributions from all CH bonds, the formation of a mixture of ethyl and "surface carbide" groups as initial species, and of *n*-butyl groups after hydrogenation would lead to the stoichiometry



and to an expected intensity ratio of 2.25, assuming all acetylenic CH becomes saturated *sp*³ CH bonds on adsorption, this ratio is not changed if the initially adsorbed alkyl species are *n*-butyl in type but depends only upon the composition assumed for the *n*-alkyl group formed after hydrogenation. For adsorption on a "hydrogen-covered" surface the intensity ratio would be 1.5 if each acetylene molecule is assumed to pick up one hydrogen atom from the metal surface.

The experimental ratios are 1.7 for "bare" nickel and 1.6 for the hydrogen-covered metal. The latter agrees with calculations within experimental error, but the observed value for the ratio on the "bare" metal is low both in absolute terms and in expectation relative to the observed ratio for "hydrogen-covered" nickel. This may mean that our method of preparing the "bare" metal leaves a partial coverage of hydrogen (12). However in view of the various assumptions made we can only conclude that a self-hydrogenation/dehydrogenation process of initial surface adsorption of the type described above is in reasonable agreement with the observed experimental data. Also, in marked contrast to the case of platinum discussed below, there is no evidence for a *net* dissociation of CH bonds to form metal-

hydrogen linkages for this process would lead to higher values of experimental compared to the calculated intensity ratio.

Finally the comparatively small reduction in intensity of the surface species on pumping out the gas phase hydrogen after hydrogenation may also be accounted for by the lack of surface metal sites free of hydrocarbon residues and hence available to act as intermediates for the surface dehydrogenation process as suggested by Eischens and Pliskin (1) and Clark (5).

5.2. Adsorption on Platinum Surfaces

The spectrum obtained after initial adsorption was weak and poorly defined in this case (Fig. 4). Although the observed bands (Table 3) occurred at similar positions to those obtained on nickel, the weakness of the spectrum makes it unreliable to estimate the surface composition from the results. After hydrogenation the integrated intensity was similar to that observed on nickel and the 2917/2953 ratio suggests strongly a more highly polymerized surface alkyl group $M(CH_2)_nCH_3$ with an average value of $n \geq 4$.

From the very great intensity increase on hydrogenation it is clear that initial adsorption on this metal gives rise to a much higher proportion of "surface carbide" or other hydrogen-deficient surface groupings i.e. that a high degree of dissociative adsorption has occurred. Clark and Sheppard (4) obtained similar, but less well-resolved, spectra with acetylene on porous-glass supported platinum. The bands in the region of 3020 and 2925 cm^{-1} in the spectrum after initial adsorption may correspond to surface $MCH=CHM$ and $M_2CH-CHM_2$ groups, respectively (22), with probably the latter dominating. The bands at 2962 and 2875 cm^{-1} suggest the presence of a small proportion of CH_3 groups formed by self-hydrogenation. The high proportion of surface carbide implicit in the large intensity increase on hydrogenation also requires the initial formation of a considerable number of surface MH bonds at the expense of CH bonds. The relative ease with which the alkyl species

after hydrogenation undergo reversible hydrogenation/dehydrogenation cycles (in contrast to the results on nickel) is explicable in terms of such adjacent MH groups. The change in the 2917/2953 cm^{-1} intensity ratio on dehydrogenation (Section 4.4) implies that this process involves the gradual reduction in the number of CH_2 relative to CH_3 groups. This is as would be expected if the dehydrogenation process starts on the carbon atom directly attached to the methyl surface and gradually proceeds towards the end methyl group.

A repetition by Clark (5) of the work carried out by Little, Sheppard, and Yates (3) involving the chemisorption of acetylene on palladium supported on porous glass gave very similar results. The only difference was that weak absorptions near 2970, 2930, and 2870 cm^{-1} could be detected in the region of sp^3 hybridized CH bonds. All of these were weaker than the strongest $C=CH$ band near 3035 cm^{-1} . There was a large increased factor in intensity of about five upon hydrogenation, and the spectrum at that stage suggested the presence of surface alkyl groups with mean composition $M(CH_2)_nCH_3$ with $n \geq 4$. The spectra illustrated by Dunken, Schmidt, and Hobert (6) before and after hydrogenation are also very similar, although it is unlikely that the surface alkyl species after hydrogenation is an ethyl group as suggested by these authors; the spectrum illustrated seems more typical of an *n*-butyl group. Nash and De Sieno (7) report very weak initial spectra with acetylene on palladium.

It may be concluded that palladium is very similar to platinum in the extent of dissociative adsorption that it induces with acetylene.

5.3. Relationship of the Spectroscopic Results to the Species Postulated for Acetylene Adsorption and Hydrogenation

In his studies of acetylene hydrogenation over nickel, Sheridan (18) visualizes that the initially adsorbed species from acetylene is $MCH=CHM$. The band near 3020 cm^{-1} on nickel can be assigned to this

species but the additional bands below 3000 cm^{-1} show that self-hydrogenation also occurs during initial adsorption (1).

Although studies of the chemisorption of acetylene on supported nickel does not provide evidence for polymerized species in the gas phase, these are readily apparent in the products formed from the acetylene/hydrogen reaction over this catalyst (18). The proportion of C_2 to C_4 or higher molecular weight products varies with the reaction conditions such as temperature and excess pressure of hydrogen. For example Sheridan (18) reports 55–60% of polymerized products of empirical composition C_4H_7 from reactions carried out between 70 and 80°C. At 200–250°C he reports C_4 and C_6 as dominant products. These findings are in good general agreement with our interpretation of the spectra of the surface species obtained initially (C_2 and C_4 species) and after hydrogenation (C_4 species). On the other hand our results, and those reported earlier by Eischens and Pliskin (1), suggest that some degree of polymerization occurs before hydrogenation, in contrast to the view that it occurs only through partially hydrogenated species $\text{MCH}=\text{CH}_2$ or $\text{MCH}=\text{CH}_2\text{M}$ (18, 19).

Both the occurrence of self-hydrogenation, and the spectroscopic intensity changes recorded on hydrogenation, imply that acetylene adsorption is accompanied by dissociation.

In comparison with nickel, the spectroscopic results on platinum imply a higher degree of initial dissociation and a greater degree of polymerization of the hydrogenated product on the surface. The very large intensity increase on hydrogenation has also been interpreted above in terms of the formation of more M–H bonds by dissociative adsorption on platinum. Beec's finding (20) that acetylene hydrogenation occurs much more rapidly over platinum than over nickel is hence understandable in terms of the smaller proportional coverage of platinum sites by adsorbed hydrocarbon groupings. Morrow and Sheppard have reached somewhat similar conclusions with ethylene (23).

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