

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 92, NUMBER 23

NOVEMBER 18, 1970

Physical and Inorganic Chemistry

The Nature of Adsorbed Propylene on Zinc Oxide.

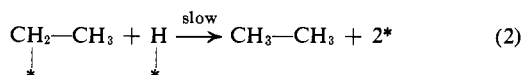
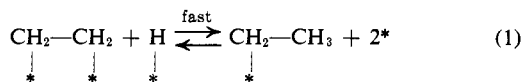
I. Formation of π -Allyl Species

A. L. Dent and R. J. Kokes*

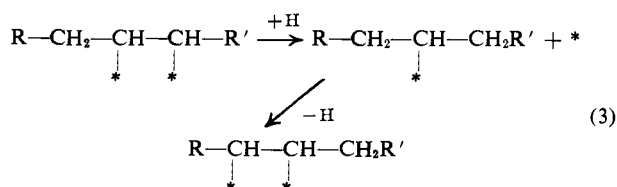
Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. Received April 27, 1970

Abstract: The infrared spectrum of chemisorbed propylene on zinc oxide has been studied with six isotopically different propylenes: $\text{CH}_3\text{—CH=CH}_2$, $\text{CD}_3\text{—CH=CH}_2$, $\text{CH}_3\text{—CD=CH}_2$, $\text{CH}_3\text{—CH=CD}_2$, $\text{CD}_3\text{—CH=CD}_2$, and $\text{CD}_3\text{—CD=CD}_2$. Adsorption yields not only a hydrocarbon spectrum but also an OH (or OD) species. Analysis of the spectrum shows that the hydrocarbon moiety formed on adsorption is an allylic species and that there is strong interaction of the double bond with the surface. Further analysis, based on the assumption that the allylic species has its geometry fixed by the surface bond but behaves as a vibrationally independent system, offers support for the view that adsorbed propylene is a species analogous to the π -allyl ligand of transition metal complexes.

Hydrogenation of ethylene over metals presumably occurs *via* the following steps



where the asterisk represents a surface atom.¹ For more complex olefins a variation on the first step offers a pathway for double-bond isomerization which often accompanies hydrogenation, *viz.*



A number of observations are consistent with this scheme; for example, we find: (a) active catalysts

* Address correspondence to this author.

(1) For a comprehensive review, see (a) G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962; (b) G. C. Bond and P. B. Wells, *Advan. Catal. Relat. Subj.*, **15**, 257 (1964).

for ethylene hydrogenation also catalyze $\text{H}_2\text{—D}_2$ equilibration, which suggests that hydrogen adsorbs as atoms, in agreement with (1) and (2); (b) reaction of light ethylene with deuterium leads to ethanes with the formula $\text{C}_2\text{H}_{6-2}\text{D}_x$, which suggests that step 1 is indeed reversible; (c) efficient isomerization of olefins requires hydrogen as a cocatalyst as suggested in (3).² Closer scrutiny of isomerization, hydrogenation, and related exchange studies reveals defects in the above picture.^{3,4} Rooney and Webb⁴ have suggested that these defects can be overcome if we assume olefins form π or π -allyl surface complexes on the metal surface. Despite the appeal of this suggestion, the most powerful technique available for studies of the nature of surface species, infrared spectroscopy, yields no evidence for π -bonded species and in fact supports the view that the surface species formed by olefins on nickel are largely paraffinic.^{5,6} Thus, despite its shortcomings, the

(2) With most group-VIII metals isomerization of butenes in the presence of hydrogen is two or more orders of magnitude faster than in the absence of hydrogen: J. Bartek, Thesis, The Johns Hopkins University, 1970.

(3) W. M. Hamilton and R. L. Burwell, Jr., *Actes Congr. Int. Catal.*, **2nd**, 1960, **1**, 987 (1961).

(4) J. J. Rooney and G. Webb, *J. Catal.*, **3**, 488 (1964).

(5) R. P. Eischens and W. A. Pliskin, *Advan. Catal. Relat. Subj.*, **10**, 1 (1958).

Table II. Adsorption of Propylene

Pretreatment	Vol ^a adsorbed, cm ³ /g	Adsorption time	Vol ^b chemisorbed, cm ³ /g	Vol ^c desorbed, cm ³ /g	Desorption conditions time, hr: temp, °C
O ₂ -500°	0.52	5 min	0.37	0.38	1:25
O ₂ -RT					1:70
O ₂ -500°	0.56	4 hr	0.39	0.37	1:140
O ₂ -RT					3:125
H ₂ -300°	0.51	4 hr	0.36	0.36	1.5:125
Vacuum-500°					
O ₂ -RT					
Vacuum-450°	0.54	4 hr	0.37	0.36	1.5:125

^a The total volume adsorbed at 21 ± 1 mm in the time indicated. ^b The volume of chemisorbed material on the surface after pumping on the sample for 10 min. ^c The volume of chemisorbed propylene recovered by collection in a liquid nitrogen trap following the schedule outlined in the last column.

hydrogen at 3489 and 1709 cm⁻¹ are quite strong; these are usually assigned to OH and ZnH species.^{9,10} In the presence of ethylene these bands shift; typically the OH band shifts upward by about 25 cm⁻¹ and the ZnH band shifts downward by about 50 cm⁻¹. As noted earlier^{9,10} these bands correspond to a relatively weak, reversible form of hydrogen chemisorption (type I) and disappear after a brief evacuation. When a catalyst containing preadsorbed propylene is exposed to hydrogen, no additional bands near 3500 and 1700 cm⁻¹ are observed that are ascribable to hydrogen chemisorption. Apparently, adsorbed propylene blocks out nearly all the sites capable of adsorbing the type-I hydrogen responsible for the ZnH and OH bands.

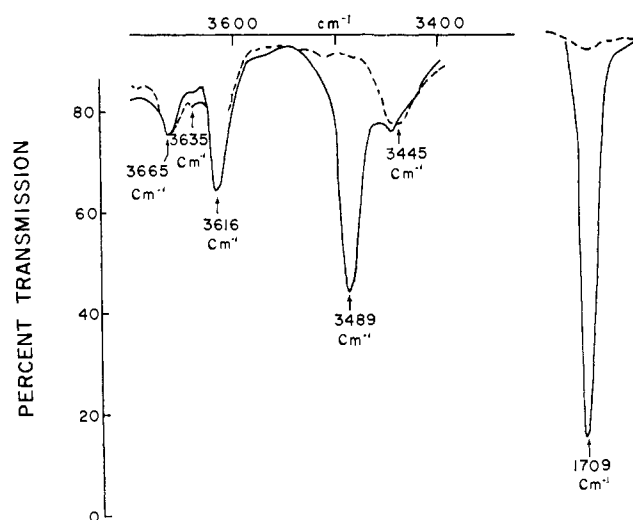
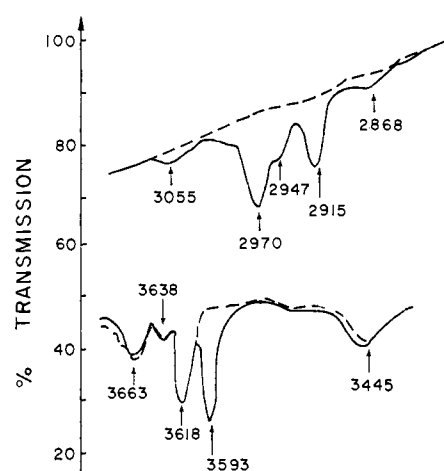


Figure 1. Spectrum of adsorbed hydrogen on zinc oxide.

Propylene Adsorption. Table II summarizes a series of measurements of propylene adsorption on a 5.0-g sample of zinc oxide at room temperature. The first column summarizes the pretreatment. In the first two runs the pretreatment is that typically used for infrared studies; for the last two runs the pretreatments are variants on pretreatments used in previous studies.^{9,10} Details of this study reveal adsorption at 20 mm was essentially complete in 3 min and was 0.51–0.56 cm³/g. About one-third of the adsorbed propylene was removed by pumping for 10 min (with a trap im-

(12) As in an earlier paper¹⁰ we shall restrict the term hydroxyl group to those bands visible in the background. The term OH and OD group shall be used to refer to species formed on on adsorption.

mersed in liquid nitrogen); the adsorbed propylene left on the surface at this point (column 4) is termed chemisorbed propylene. The amount of chemisorbed propylene appears to be independent of pretreatment or the length of time propylene is exposed to the catalyst. This chemisorbed propylene cannot be removed even by several hours of pumping at room temperature. Column 5 lists the amounts of gas collected by pumping through a liquid nitrogen trap with the heating schedule specified in the last column. These data suggest that the chemisorbed gas is recovered quantitatively by this procedure. Chromatographic analysis of the recovered gas reveals that it is 99.9% propylene with about 0.1% propane and no dimeric product.

Figure 2. Spectrum of chemisorbed propylene (CH₃-CH=CH₂).

Adsorbed propylene is dramatically different from adsorbed ethylene insofar as the former requires degassing at elevated temperatures whereas the latter is readily removed by brief degassing at room temperature.¹³ Thus, the bonding of adsorbed propylene to the surface seems much stronger than that for adsorbed ethylene. Furthermore, it should be noted that a monolayer of propylene on this catalyst (assuming a cross section of 25–30 Å²) would be 1.1–1.3 cm³/g. Thus, the strong propylene adsorption (0.37 cm³/g) occurs on only a limited number of sites.

Infrared Spectrum of Adsorbed Propylene. The spectrum of chemisorbed propylene in the CH and O-H stretching is shown in Figure 2. The band at 3593

(13) A. L. Dent and R. J. Kokes, unpublished results.

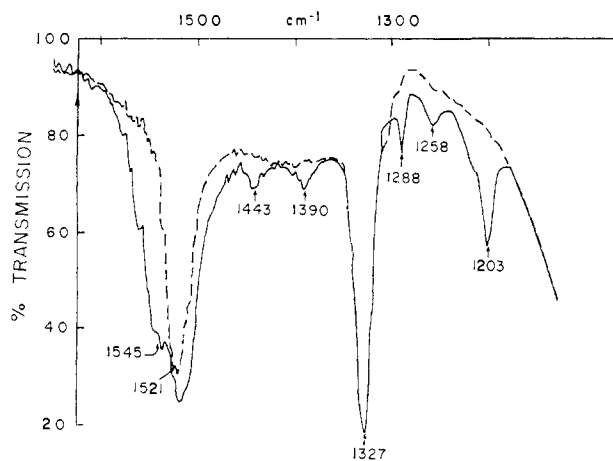
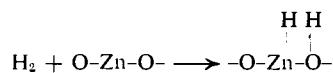
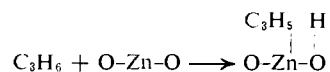


Figure 3. Spectrum of chemisorbed propylene ($\text{CH}_3\text{-CH=CH}_2$).

cm^{-1} can be reasonably assigned only to an OH frequency; hence, it appears that dissociation accompanies propylene adsorption. Careful scrutiny of the region from 1500 to 2000 cm^{-1} reveals no band assignable to a ZnH band. Since the presence of adsorbed propylene blocks out the infrared active hydrogen chemisorption on the ZnO pair sites, *i.e.*



we may assume that propylene adsorption occurs as follows



In this picture the hydrocarbon fragment blocks out the zinc half of the active site; hence, the ZnH band is not observed. The frequency of the OH band formed from propylene is about 105 cm^{-1} higher than that for adsorbed hydrogen. We have already noted, however, that the OH band from adsorbed hydrogen shifts upward about 25 cm^{-1} in the presence of the weakly bound ethylene; the larger upward shift in the presence of the more strongly held propylene is therefore not unexpected.

Five bands are observed in the region near 3000 cm^{-1} corresponding to C-H stretching vibrations. (The band at 2947 cm^{-1} , which appears as a shoulder in Figure 2, is seen as a separate peak when the spectrum is observed on an expanded transmission scale.) Detailed identification of these bands will be deferred, but the weak band at 3055 cm^{-1} suggests that the hydrocarbon fragment is olefinic. (Usually, paraffinic C-H stretches occur below 3000 cm^{-1} .⁶)

Figure 3 shows the spectrum of chemisorbed propylene in the C-H deformation region. In this region the background spectrum for zinc oxide has two strong bands at 1521 and 1327 cm^{-1} . These bands are observed in all samples of zinc oxide;¹⁴ they seem to arise from residual carbon dioxide and are most important in this work for their nuisance value. Bands observed between 1450 and 1200 cm^{-1} can reasonably be assigned to C-H deformation vibrations, but there are one or

more bands almost on top of the background band at 1521 cm^{-1} . One could interpret this band as the result of broadening and enhancement of the background band, but we view it as a band due to the hydrocarbon with a maximum at 1545 cm^{-1} accompanied by a background band slightly shifted to lower frequencies. A band at 1545 cm^{-1} cannot be due to C-H vibrations unless we postulate some curious kind of overtone. This band, however, does correspond to a carbon-carbon stretch with appreciable olefinic character. Coupled with the evidence of olefinic character in the C-H stretching region this assignment seems reasonable. In the gas phase, the double-bond stretch for propylene occurs at 1652 cm^{-1} ;¹⁵ hence, interaction of the double bond with the surface has shifted the stretching frequency by 107 cm^{-1} . This suggests that π bonding is involved in the chemisorption of propylene.

If the spectrum of adsorbed propylene is observed in the presence of gaseous propylene, additional bands to those shown in Figures 2 and 3 are observed. These additional bands are due to a more weakly bound form of propylene which is readily removed by a brief evacuation. The salient feature of the spectrum of the weakly bound propylene is a band of 1620 cm^{-1} . This band, clearly in the double-bond stretching region, is about 30 cm^{-1} lower than that for liquid propylene, a shift too large to be accounted for by nonspecific physical adsorption. A similar shift is observed in the spectrum of adsorbed ethylene, and in this case heat measurements show the ethylene is chemisorbed;¹³ hence, it seems reasonable to conclude that the bonding of this weakly held propylene is the analog of that found for chemisorbed ethylene. Shifts of double-bond frequencies to lower values are encountered when olefins form π complexes with metal ions in solution^{16,17} or with cations in molecular sieves;¹⁸ hence, we shall refer to this weakly bound propylene as a surface π complex.

There appears to be a one-to-one correspondence between the species responsible for the ir bands and the chemisorbed species as defined in Table II. In particular: (1) the spectrum characteristic of the dissociatively adsorbed species is fully developed a few minutes after the sample is exposed to propylene; (2) evacuation at room temperature for several hours has no effect on the spectrum of the strongly held propylene; (3) degassing for 1.5 hr at 125° brings about complete disappearance of the bands due to adsorbed propylene, including the OH band formed on adsorption; and (4) qualitative observations of the band intensities during degassing suggest that all bands disappear at the same rate. These observations suggest that the chemisorbed propylene, defined as in Table II or by the ir bands, is essentially a single species.

Spectrum of Adsorbed Perdeuteriopropylene. Figure 4 shows the spectrum for chemisorbed C_3D_6 in the OH stretching region ($\sim 3500 \text{ cm}^{-1}$), the OD stretching region ($\sim 2600 \text{ cm}^{-1}$), and the C-D stretching region. Near 3500 cm^{-1} we find only slight changes in the background hydroxyl bands, which may be perturbations due to the adsorbed olefin. At 2653 cm^{-1} , however,

(15) R. C. Lord and P. Venkataswarlu, *J. Opt. Soc. Amer.*, **43**, 1079 (1953).

(16) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958).

(17) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2896 (1965).

(18) J. L. Carter, D. J. C. Yates, P. J. Lucchesi, J. J. Elliot, and V. Kevorkian, *J. Phys. Chem.*, **70**, 1126 (1966).

(14) See, for example, J. H. Taylor, and C. H. Amberg, *Can. J. Chem.*, **39**, 535 (1961); C. H. Amberg and D. H. Seanor, *Proc. Int. Congr. Catal.*, **3rd**, **1**, 450 (1964).

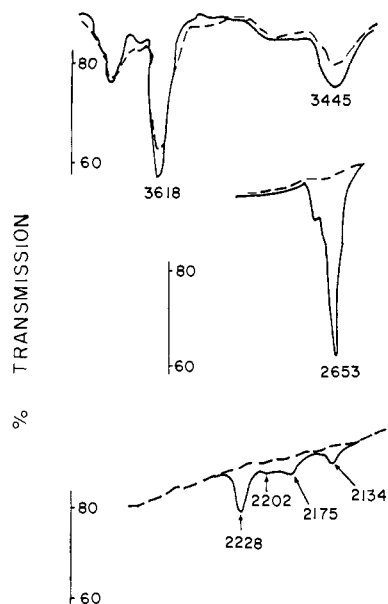


Figure 4. Spectrum of chemisorbed propylene ($\text{CD}_3\text{-CD}=\text{CD}_2$).

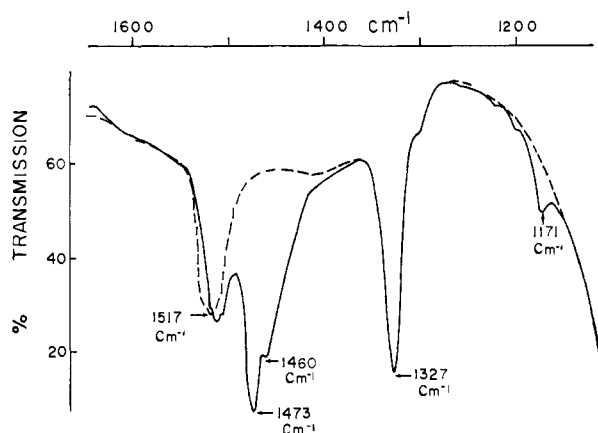


Figure 5. Spectrum of chemisorbed propylene ($\text{CD}_3\text{-CD}=\text{CD}_2$).

we see a strong band (with some structure) that can only be assigned to an OD formed by the adsorption of propylene. (It may be thought that this band might arise from exchange with surface hydroxyls. Three features of these studies rule this out: (a) the OD band forms essentially instantaneous and does not change with time; (b) the surface hydroxyls change little in intensity; and (c) a surface deuterioxy band is evident on a sample previously exposed to perdeuteriopropylene, but it is very weak. Thus, these observations support the view that propylene adsorbs dissociatively.)

Figure 4 also shows the spectrum of chemisorbed C_3D_6 in the C-D stretching region. Four weak bands are observed. The band at 2202 cm^{-1} is very weak but scans on an expanded transmission scale confirm its presence. From the data for adsorbed C_3H_6 and the isotopic shifts encountered for gaseous C_3H_6 and C_3D_6 , one would expect an additional band at about 2280 cm^{-1} corresponding to the 3055-cm^{-1} absorption of C_3H_6 . Repeated scans under a variety of experimental conditions failed to reveal a definite band in this region. This result, while frustrating, is not surprising; the band at 3055 cm^{-1} is very weak and broad in the rather strong

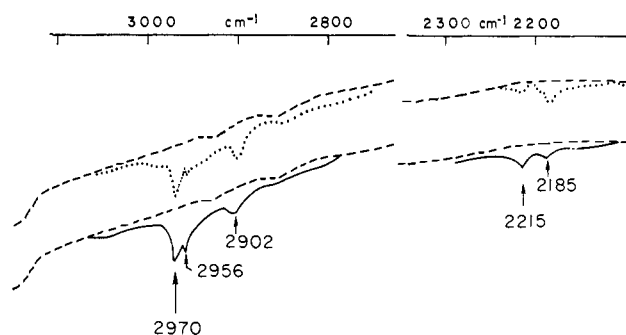


Figure 6. Spectrum of chemisorbed propylene ($\text{CD}_3\text{-CH}=\text{CH}_2$ and $\text{CH}_3\text{-CH}=\text{CD}_2$): \cdots , chemisorbed $\text{CD}_3\text{-CH}=\text{CH}_2$ on zinc oxide; --- , chemisorbed $\text{CH}_3\text{-CH}=\text{CD}_2$ on zinc oxide.

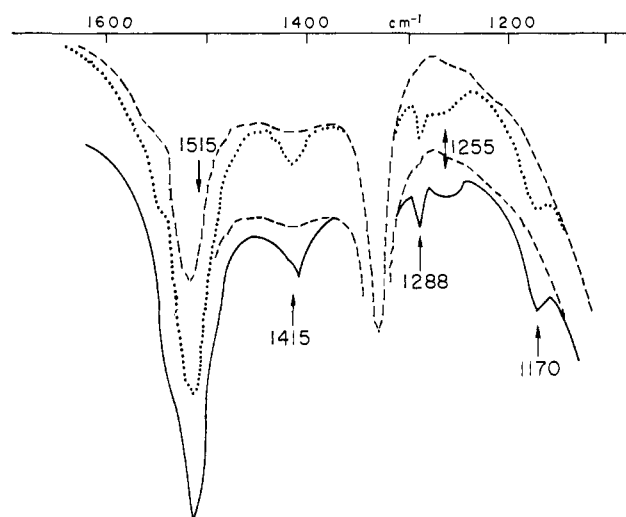


Figure 7. Spectrum of chemisorbed propylene ($\text{CD}_3\text{-CH}=\text{CH}_2$ and $\text{CH}_3\text{-CH}=\text{CD}_2$): \cdots , chemisorbed $\text{CD}_3\text{-CH}=\text{CH}_2$ on zinc oxide; --- , chemisorbed $\text{CH}_3\text{-CH}=\text{CD}_2$ on zinc oxide.

C_3H_6 spectrum; in the less intense C_3D_6 spectrum the band near 2280 cm^{-1} would be expected to be so weak that it would be difficult to observe.

Figure 5 shows the spectrum of C_3D_6 in the CH deformation region. We would expect the normal isotope effect to shift C-D deformations about 400 cm^{-1} , that is, completely out of this region. Thus, the observed bands are due to C-C vibrations. The band at 1473 (with a shoulder at 1460) can only correspond to the 1545-cm^{-1} band in C_3H_6 . The isotope shift, 68 cm^{-1} , is very nearly the same as the isotope shift of the C=C frequency (70 cm^{-1}) for the gas-phase spectra;¹⁵ hence, the position of this band substantiates our previous conclusion that the 1545-cm^{-1} band is the double-bond frequency shifted by adsorption. In addition, the spectrum in Figure 5 shows more clearly that the background band at about 1525 is shifted to lower frequencies by the adsorption of propylene.

Spectrum of Labeled Propylenes. The spectra of C_3H_6 and C_3D_6 show that chemisorption of propylene is dissociative, but they fail to identify which carbon-hydrogen bond is broken on adsorption. To this end the spectra of a number of deuterium-labeled propylenes were studied and compared. These results are summarized in Table III and Figures 6-9. The data in Table III specify the hydrogen fragment formed on adsorption; the fragment was identified as an OH if a

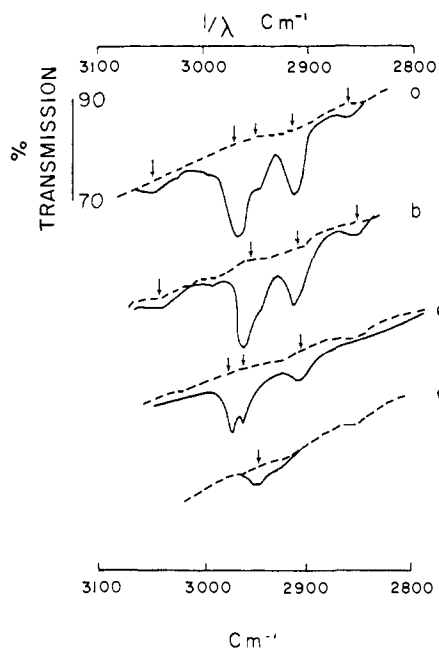


Figure 8. Spectrum of chemisorbed propylenes in the C-H stretching region: (a) chemisorbed $\text{CH}_3\text{-CH=CH}_2$ on zinc oxide, (b) chemisorbed $\text{CH}_3\text{-CD=CH}_2$ on zinc oxide, (c) chemisorbed $\text{CD}_3\text{-CH=CH}_2$ on zinc oxide, (d) chemisorbed $\text{CD}_3\text{-CH=CD}_2$ on zinc oxide.

band appeared near 3593 cm^{-1} or as an OD if a band appeared near 2653 cm^{-1} . In those cases where the spectrum changed with time the summary in Table III applies to the initial spectrum. These results show that the dissociative adsorption of propylene occurs by cleavage of a methyl carbon-hydrogen bond to form an allylic species.

Table III. Spectrum of Chemisorbed Propylenes

Compound	Surface fragment	Spectrum
I $\text{CH}_3\text{-CH=CH}_2$	O-H	Stable
II $\text{CD}_3\text{-CD=CD}_2$	O-D	Stable
III $\text{CH}_3\text{-CD=CH}_2$	O-H	Stable
IV $\text{CH}_3\text{-CH=CD}_2$	O-H	Changes
V $\text{CD}_3\text{-CH=CH}_2$	O-D	Changes
VI $\text{CD}_3\text{-CH=CD}_2$	O-D	Stable

Figures 6 and 7 show the spectra of chemisorbed $\text{CH}_3\text{-CH=CD}_2$ (IV) and $\text{CD}_3\text{-CH=CH}_2$ (V) in the C-H stretching and deformation region. The wavelength scale is the same, but for clarity the transmission scales for the two spectra have been shifted. Although IV yields an OH fragment on adsorption and V yields an OD fragment on adsorption, the initial spectra of the surface hydrocarbons formed by these two compounds are the same within experimental error. (In time these spectra change so that they are no longer identical; the nature of these changes and their interpretation are discussed in the next paper.) The coincidence of the initial hydrocarbon spectrum for adsorbed IV and V strongly suggests that propylene adsorbs to form a symmetric allylic species

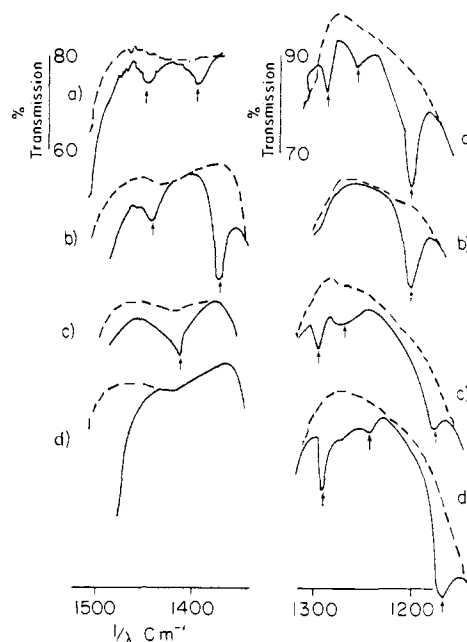
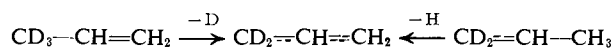
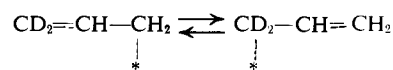


Figure 9. Spectrum of chemisorbed propylenes in the C-H deformation region: (a) chemisorbed $\text{CH}_3\text{-CH=CH}_2$ on zinc oxide, (b) chemisorbed $\text{CH}_3\text{-CD=CH}_2$ on zinc oxide, (c) chemisorbed $\text{CD}_3\text{-CH=CH}_2$ on zinc oxide, (d) chemisorbed $\text{CD}_3\text{-CH=CD}_2$ on zinc oxide.

It is conceivable that IV and V both yield two rapidly equilibrating species, *i.e.*



and that Figures 6 and 7 represent the composite spectrum, but the spectrum itself makes this interpretation unlikely. The two equilibrating species would give rise to six C-H and four C-D stretches; nature is not so vindictive that it would combine overlap and intensity of these ten bands to yield the three C-H and two C-D bands expected for the symmetric species.

Group Frequencies. Given the assumption that a symmetric allyl species is formed on adsorption, we can make reasonably straightforward assignments of group frequencies (Table IV). Figures 8 and 9 show a comparison of the spectra in the C-H stretching and deformation region for four labeled propylenes. Band positions are marked by arrows. We have adopted the operating principle that a band is present only if it shows a maximum either on the standard-scale spectrum or on the expanded scale; this means asymmetric peaks with only one maximum will be treated as a single band.

For the C-H stretching region of the $\text{CH}_2\text{-CH-CH}_2$ we expect five bands. One of these corresponds to the CH stretch of the center carbon atom. The two CH_2 groups are coupled *via* the central carbon atom; hence, we can expect each of the two stretches characteristic of isolated CH_2 groups (symmetric and antisymmetric) to split into two bands corresponding to in-phase and out-of-phase vibrations. The five-band spectrum in Figure 8a is consistent with this reasoning. For the species $\text{CH}_2\text{-CD-CH}_2$ (Figure 8b) we find a four-band spectrum. The band that disappeared is the central C-H stretch (at 2947 cm^{-1}), and the remaining four

Table IV. Group Frequencies (cm^{-1}) of Isotopic Adsorbed Propylenes^a

Assignment ^b	A	B	C	D	E ^c	F
OH, OD	3593 (95)	3593 (74)	3593 (79)	2653 (51)	2653 (55)	2653 (68)
CH ₂ (c) or CD ₂ (c)	3055 (3)	3045 (4)			(2280) ^d	(2280) ^d
CH ₂ (u)			2970 (20)	2970 (20)		
CD ₂ (u)			2215 (5)	2218 (3)		
CH ₂ (c) or CD ₂ (c)	2970 (31)	2960 (32)			2222 (11)	2228 (15)
CH or CD	2947 (8)	2202 (11)	2957 (6)	2955 (5)	2950 (5)	2202 (2)
CH ₂ (c) or CD ₂ (c)	2915 (21)	2913 (20)			2178 (10)	2175 (7)
CH ₂ (u)			2904 (9)	2902 (10)		
CD ₂ (u)			2185 (3)	2187 (6)		
CH ₂ (c) or CD ₂ (c)	2868 (3)	2855 (3)			2125 (5)	2134 (6)
C-C (c)	1545 (103)	1525 (131)	1515 (98)	1515 (104)	1502 (153)	1473 (148)
CH ₂ ^e (c)	1443 (15)	1435 (17)				
CH ₂ ^e (u)			1409 (20)	1415 (15)		
CH ₂ ^e (c)	1390 (12)	1369 (52)				
C-H ^e	1288 (28)		1288 (30)	1288 (26)	1288 (35)	
C-H ^e	1258 (12)		1255 (13)	1265 (11)	1245 (9)	
C-C (c)	1203 (51)	1203 (29)	1170 (34)	1170 (24)	1159 (24)	1171 (18)

^a Numbers in parentheses after frequencies are relative extinction coefficients. Errors in the position of band centers depend on the band shape; normally, the accuracy is about 3 cm^{-1} or better. Column A refers to the process $\text{CH}_3\text{-CH=CH}_2 \rightarrow \text{OH} + \text{CH}_2\text{CHCH}_2$; B to $\text{CH}_3\text{-CD=CH}_2 \rightarrow \text{OH} + \text{CH}_2\text{CDCH}_2$; C to $\text{CH}_3\text{-CH=CD}_2 \rightarrow \text{OH} + \text{CH}_2\text{CHCD}_2$; D to $\text{CD}_3\text{-CH=CH}_2 \rightarrow \text{OD} + \text{CD}_2\text{CHCH}_2$; E to $\text{CD}_3\text{-CH=CD}_2 \rightarrow \text{OD} + \text{CD}_2\text{CHCD}_2$; and F to $\text{CD}_3\text{-CD=CD}_2 \rightarrow \text{OD} + \text{CD}_2\text{CDCD}_2$. ^b Letters in parentheses indicate whether vibrations of a fragment are coupled (c) to vibrations of a similar fragment or uncoupled (u). ^c A very weak band appears at 2202 cm^{-1} for which we have no assignment. ^d The C-D bands are in general weaker than corresponding C-H bands; hence, it is not surprising that the CD band corresponding to the weak 3055-cm^{-1} CH band is not observed. The numbers given are estimates based on isotopic shifts found in the gas phase. They should be good to about 20 cm^{-1} . Corresponding C-D bands are expected below 1150 cm^{-1} , where zinc oxide becomes essentially opaque.

bands represent the coupled CH₂ vibrations. For the species CD₂-CH-CH₂ (Figure 8c) we find a three-band spectrum. One of these bands represents the central C-H stretch and the other two represent uncoupled CH₂ stretches. The shapes and positions of these bands suggest that the other bands, at 2970 and 2902 cm^{-1} , represent the uncoupled CH₂ vibrations and the middle band at 2956 cm^{-1} corresponds to the center C-H stretch. A check of this description is supplied by the spectrum of CD₂-CH-CD₂ (Figure 8d), which shows a single C-H stretch at 2950 cm^{-1} , the region already deduced to be characteristic of the central C-H stretch.

Similar analysis can be applied to the spectrum in the deformation region (Figure 9). The two bands in the $1400\text{-}1500\text{-cm}^{-1}$ region of propylene (Figure 9a) appear to be due to in-phase and out-of-phase in-plane deformations of CH₂. Two bands are still observed in the spectrum of CH₂-CD-CH₂ (Figure 9b), but they coalesce to form a single band characteristic of an uncoupled CH₂ group in the spectrum of CD₂-CH-CH₂ (Figure 9c). As expected no bands in this region are observed for CD₂-CH-CD₂ (Figure 9d).

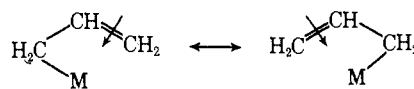
The spectrum of propylene in the $1300\text{-}1150\text{-cm}^{-1}$ region shows three bands. The lowest of these bands appears for all the propylenes, including perdeuterio-propylene; hence, it is most likely a carbon-carbon vibration. Comparison of the spectra in Figure 9 shows that the upper two bands are associated with the vibration of the hydrogen on the center carbon. Presumably, the higher frequency in propylene (1288 cm^{-1}) represents in-plane bending and the lower frequency (1258 cm^{-1}) represents the out-of-plane bending. In gaseous propylene the out-of-plane bending frequency (990 cm^{-1}) is much lower; hence, this last group frequency assignment is somewhat surprising, but comparison of spectra leaves us with no other choice.

Similar reasoning to the above provides us with group frequency assignments for C-D and C-C vibrations. We have listed these assignments in Table IV.

Discussion

The results suggest that propylene on chemisorption forms a symmetric allylic species with π bonding to the surface. For a surface π allyl, we would expect gross similarities to known π -allyl complexes of transition metals. Data for allyl complexes of manganese carbonyls¹⁹ show that for the σ -allyl species the double-bond frequency occurs at about 1620 cm^{-1} ; formation of the π -allyl species causes a much larger double-bond frequency shift to 1505 cm^{-1} . The shift we observe (to 1545 cm^{-1}) seems too large for a simple σ complex, but is less than that observed for transition metal π allyls. Since for simple π complexes there is a correlation of bond strength to double-bond frequency shift,^{18,20} we believe that the observed shift suggests a weaker bonding for the surface complex than that found for transition metal complexes.

Bonding of the π -allyl ligand to the metal²¹ can be viewed as follows



wherein the plane of the three carbons is nearly perpendicular to the metal-allyl bond axis, with a slight tilt so that the end carbon atoms are closer to the metal than the central carbon atom. Although X-ray studies suggest the two carbon-carbon bonds are not quite the same length,²² the validity of this conclusion has been questioned.²³ In either case, to a first approximation, the allyl ligand in π allyls has the form

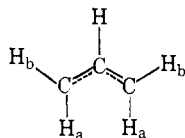
(19) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).

(20) H. W. Quinn and D. N. Glav, *Can. J. Chem.*, **40**, 1103 (1962).

(21) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Stehrucke, D. Walter, and H. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **5**, 151 (1966).

(22) R. Mason and D. R. Russell, *Chem. Commun.*, 26 (1966).

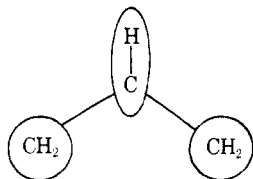
(23) F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, **6**, 179 (1967).



The nmr studies indicate that the hydrogen atoms labeled a, which interact more strongly with metal, are more paraffinic than the hydrogen atoms labeled b. We believe the surface species has this form, with the zinc atom of the active site playing the role of the metal. Note that this suggested structure is symmetric, as implied by the identity of the hydrocarbon spectra of adsorbed $\text{CD}_3\text{—CH=CH}_2$ and $\text{CH}_3\text{—CH=CD}_2$.

Fischer and Werner²⁴ have listed the infrared spectra of a number of π -allyl complexes. Band positions due to the π -allyl ligand shift considerably from one metal to another. Accordingly, it is pointless to attempt to test our identification by further comparison to these spectra. Instead we shall base our analysis on the following view. The bonding to the surface determines the geometry, force constants, etc. of the adsorbed hydrocarbon fragment. Once these are fixed, however, the hydrocarbon fragment behaves vibrationally as a separate entity because the low-frequency allyl-surface vibrations couple only loosely with the hydrocarbon frequencies.²⁵ This view, admittedly a rough approximation, is similar to the view used to justify the "constancy" of group frequencies;²⁶ now, however, we are taking the whole adsorbed species as a complex "group frequency." On this basis, the vibrations of the surface π allyl are those expected for a molecule with C_{2v} symmetry.

Consider first the carbon-carbon vibrations. We shall assume, as is often done,²⁷ that the hydrogen atoms move in concert with the carbons in these vibrations so that the molecule is essentially a symmetric bent triatomic of the form



Such a molecule, with ankylosed CH bonds, has three normal modes: symmetric stretching, ν_1' ; bending, ν_2' ; and asymmetric stretching, ν_3' . The equations for valence-force calculations (given in Herzberg²⁷) show that the vibration frequencies depend on the bond angle, the stretching force constant, and the bending force constant. The form of the equations is such that the frequencies ν_3' and ν_1' are sensitive to the angle and stretching force constant but not sensitive to the bending force constant. On the basis of our structural assignment, the bond angle should be about 120° . We shall further assume that ν_2' is the same as that for propylene, 417 cm^{-1} .²⁸ If we fix the stretching force

constant by assigning the 1545-cm^{-1} band for adsorbed propylene to ν_3' , we can compute with no further assumptions the positions of ν_1' for adsorbed propylene and both ν_1' and ν_3' for all other symmetric deuterium isomers. These calculations and their comparison to experiment are shown in Table V.

Table V. Calculated vs. Observed Carbon-Carbon Frequencies

Molecule	Vibration ^a	Exptl	Calcd ^b	% error
C_3H_6	ν_3'	1545		
	ν_1'	1203	1208	0.4
$\text{C}_3\text{H}_5\text{D}$	ν_3'	1525	1517	0.5
	ν_1'	1203	1208	0.9
$\text{C}_3\text{D}_5\text{H}$	ν_3'	1502	1504	0.1
	ν_1'	1159	1162	0.3
C_3D_6	ν_3'	1473	1470	0.2
	ν_1'	1170	1147	2.0

^a The numbering of frequencies is that of Herzberg for a triatomic with C_{2v} symmetry. ^b The ν_3' frequency for adsorbed C_3H_6 used to compute the stretching force constant with the assumption that the bond angle was 120° and the C-C-C bending frequency was the same as that for propylene.

In order to test the sensitivity of the model, calculations were repeated with the assumed value of $\nu_2' = 517\text{ cm}^{-1}$. This increase of 24% in the value of ν_2' caused ν_1' to increase to 1220 cm^{-1} , a 1% change in frequency. By way of contrast, if the angle was changed by 4%, the change in the calculated value of ν_1' was 50 cm^{-1} (4%). Thus, the calculations provide a sensitive test of the assumed geometry.

The value of the stretching force constant is $7.54 \times 10^5\text{ dyn/cm}$. This is about midway between typical values²⁶ for single and double bonds and comparable to that found for C_6H_6 ; hence, this value, indicative of one-half double-bond character, also suggests a π allyl species.

Now consider the remaining frequencies. For a π allyl with C_{2v} symmetry the 18 vibrations²⁹ consist of 7 vibrations ($\nu_1\text{--}\nu_7$) of type A_1 , 2 vibrations (ν_8 and ν_9) of type A_2 , 6 vibrations ($\nu_{10}\text{--}\nu_{15}$) of type B_1 , and 3 vibrations ($\nu_{16}\text{--}\nu_{18}$) of type B_2 . (The numbering of frequencies is that suggested by Herzberg.³⁰) For strict C_{2v} symmetry all species except A_2 would be infrared active, but the field of the surface probably makes even the A_2 species infrared active. By the use of symmetry coordinates reasonable associations of the group frequencies in Table IV can be made to various symmetry species. For example, of the five C-H stretching frequencies, three are of species A_1 and two are of species B_1 . The three A_1 species can be taken as a CH stretch of the central carbon atom and two coupled in-phase vibrations of the CH_2 groups. The two B_1 species can be taken as the two out-of-phase vibrations of CH_2 groups. Asymmetric CH_2 stretches generally occur at higher frequencies than the symmetric stretches.³¹ When they are coupled, as in ethylene,³² the in-phase stretching vibrations generally occur at higher frequencies than the out-of-phase vibrations. If we assume the same behavior for the π -allyl species, we can associate all of the frequencies

(24) E. O. Fischer and H. Werner, "Metal π -Complexes" Elsevier, Amsterdam, 1966, pp 182-183.

(25) A similar view applied to π -allyl complexes is taken by H. P. Fritz, *Chem. Ber.*, **94**, 1217 (1961).

(26) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945, pp 192-201.

(27) Reference 26, pp 168-175.

(28) Reference 26, p 355.

(29) Reference 26, p 132.

(30) Reference 26, p 272.

(31) Reference 6, pp 4-5.

(32) Reference 26, p 326.

Table VI. Assignments for Adsorbed C₃H₆

Frequency, cm ⁻¹	Species	Comment ^b
3055	A ₁	ν_1 in-phase CH ₂ (anti)
2970	B ₁	ν_{10} out-of-phase CH ₂ (anti)
2947	A ₁	ν_2 C-H stretch
2915	A ₁	ν_3 in-phase CH ₂ (sym)
2868	B ₁	ν_{11} out-of-phase CH ₂ (sym)
1545	B ₁	ν_{12} C-C stretch (anti)
1443	B ₁	ν_{13} out-of-phase CH ₂ in-plane
1390	A ₁	ν_4 in-phase CH ₂ in-plane
1288	B ₁	ν_{14} CH in-plane
1258	B ₂	ν_{16} C-H out-of-plane
1203	A ₁	ν_5 C-C-C stretch (sym)
1100 ^a	A ₁	ν_6 in-phase CH ₂ wag
1000 ^a	B ₁	ν_{15} out-of-phase CH ₂ wag
950 ^a	A ₂	ν_8 in-phase CH ₂ rock
950 ^a	B ₂	ν_{17} out-of-phase CH ₂ rock
800 ^a	A ₂	ν_9 in-phase CH ₂ twist
800 ^a	B ₂	ν_{18} out-of-phase CH ₂ twist
417 ^a	A ₁	ν_7 C-C-C bend

^a Estimated frequencies for bands not observed. ^b Frequencies numbered following the convention used by Herzberg.³⁰

listed in Table IV to a particular species. This is done in Table VI along with a one-word description of the nature of the vibration. In addition to identifying observed bands, we have included estimates, based on group frequencies of similar molecules, of the expected position of bands not seen. It can be seen that those bands not seen are expected at frequencies below 1150 cm⁻¹, a region where zinc oxide becomes opaque.

Shifts of frequencies for isotopic species provide a sensitive test of an assignment.^{33,34} The sum rules of Decius and Wilson,³⁴ which require three or more isotopic species, are particularly suitable for the present case. These rules state that if we write equations of the forms

$$\text{CH}_2\text{-CD-CH}_2 + \text{CD}_2\text{-CH-CD}_2 = \text{CD}_2\text{-CD-CD}_2 + \text{CH}_2\text{-CH-CH}_2 \quad (5)$$

$$\text{CD}_2\text{-CH-CH}_2 + \text{CH}_2\text{-CD-CH}_2 + \text{CH}_2\text{-CH-CD}_2 = 2\text{CH}_2\text{-CH-CH}_2 + \text{CD}_2\text{-CD-CD}_2 \quad (6)$$

sums of squares of the frequencies of symmetry species *common to all compounds* must satisfy equations of the same form. For eq 5 (with the common symmetry C_{2v}) we can write

$$\sum \nu^2(\text{CH}_2\text{-CD-CH}_2) + \sum \nu^2(\text{CD}_2\text{-CH-CD}_2) = \sum \nu^2(\text{CD}_2\text{-CD-CD}_2) + \sum \nu^2(\text{CH}_2\text{-CH-CH}_2) \quad (7)$$

and this equation holds separately for the A₁, A₂, B₁, and B₂ species. For eq 6 (where the common symmetry is C_s) we can write

$$2\sum \nu^2(\text{CD}_2\text{-CH-CH}_2) + \sum \nu^2(\text{CH}_2\text{-CD-CH}_2) = 2\sum \nu^2(\text{CH}_2\text{-CH-CH}_2) + \sum \nu^2(\text{CD}_2\text{-CD-CD}_2) \quad (8)$$

and this sum will apply to the A' and A'' species separately. The advantage of this form for present applications is that because it involves the sums of *squares* of frequencies, the low-frequency terms make only a small contribution to the overall sums. Rough estimates show that we should be able to omit frequencies below 1150 cm⁻¹ for the A₁ and B₁ sums in eq 7

(33) Reference 26, pp 231-238.

(34) J. C. Decius and E. B. Wilson, Jr., *J. Chem. Phys.*, **19**, 1409 (1951).

Table VII. Symmetry Species and Positions (cm⁻¹) of Bands Used for Sum Rules

CH ₂ - CHCH ₂	CH ₂ - CDCH ₂	CD ₂ - CHCD ₂	CD ₂ - CDCD ₂	CD ₂ - CHCH ₂ ^b
3055 (A ₁)	3045 (A ₁)	2950 (A ₁)	2280 ^a (A ₁)	2970 (A')
2947 (A ₁)	2913 (A ₁)	2280 ^a (A ₁)	2202 (A ₁)	2956 (A')
2915 (A ₁)	2202 (A ₁)	2178 (A ₁)	2175 (A ₁)	2903 (A')
1390 (A ₁)	1369 (A ₁)	1159 (A ₁)	1171 (A ₁)	2216 (A')
1203 (A ₁)	1203 (A ₁)	2222 (B ₁)	2228 (B ₁)	2186 (A')
2970 (B ₁)	2960 (B ₁)	2125 (B ₁)	2134 (B ₁)	1514 (A')
2868 (B ₁)	2855 (B ₁)	1502 (B ₁)	1473 (B ₁)	1410 (A')
1545 (B ₁)	1525 (B ₁)	1288 (B ₁)		1288 (A')
1443 (B ₁)	1435 (B ₁)			1170 (A')
1288 (B ₁)				

^a This band, expected to be weak, is so weak it is not observed. Since the estimate seems well founded, it is included in the sums. ^b Sums involving this species have a common C_s symmetry and only A' species are sufficient in number to use. For molecules in the sum with individual C_{2v} symmetry the A₁ and B₁ species reduce to A' species.

and the A' sums in eq 8 and still have the equalities hold if the assignment is correct. Table VII lists the frequencies (above 1150 cm⁻¹) for the deuterium isomers appearing in eq 5 and 6. The sums for the left and right sides of eq 7 and 8 with missing frequencies below 1150 cm⁻¹ omitted are listed in Table VIII.

Table VIII. Test of Sum Rules^a

Equation 7, A ₁ species × 10 ⁻⁶ :	25.92 + 19.99 = 16.15 + 29.89
	45.91 = 46.04
	(0.28% error)
Equation 7, B ₂ species × 10 ⁻⁶ :	21.35 + 13.37 = 11.69 + 23.17
	34.72 = 34.86
	(0.40% error)
Equation 8, A' species × 10 ⁻⁶ :	86.00 + 47.27 = 106.12 + 27.84
	133.27 = 133.96
	(0.52% error)

^a These represent sums in which the frequencies below 1150 cm⁻¹ were not included.

The agreement for these sums is as good as that found for simple molecules by Decius and Wilson;³⁴ hence, this test offers further support for our assignments.

Detailed discussion of the nature of the sites that adsorb propylene to yield the allylic species will be deferred until the next paper. Nevertheless, a few remarks about these sites should be made. (1) Adsorbed propylene blocks out the adsorption of hydrogen that gives rise to infrared bands; hence, it would seem that propylene saturates these sites. Despite this apparent saturation, the intensity of the OH band from propylene is only about 40% of that for adsorbed hydrogen on a clean surface. Factors governing the intensity of ir bands are complex. Therefore, although the intensity of the OH band formed from adsorbed propylene is lower than expected on a simple picture, we do not believe this lower intensity should be taken as evidence that a substantial portion of the chemisorbed propylene is undissociated. (2) The estimated number of sites capable of adsorbing hydrogen to form ZnH and OH bands corresponds to only one-third the amount of propylene chemisorbed. Accordingly, we must conclude that either the estimate of the number of hydrogen active sites is low or adsorption of propylene takes place on sites other than those active for hydrogen chemisorption. (3) The band assigned to the asym-

metric carbon-carbon stretch is probably a multiple band. In most cases this band is merely broad, but for perdeuteriopropylene (Figure 5) the structure of the band is evident. This structure can be rationalized if we assume that similar but slightly different sites are involved in the chemisorption. The differences in bonding to these different sites would be more likely to manifest themselves in the carbon-carbon bond, involved in π bonding, than for the once-removed carbon-hydrogen bond. In this event, structure in the vibrational bands for the allyl species could be evident for the carbon-carbon frequencies but not for the carbon-hydrogen frequencies. This means that if we include only the most prominent carbon-carbon band (the maximum) in our analysis, we are justified in treating the spectrum as if it were that for a single species.

Finally, we should note that although the treatment of the adsorbed allyl as a vibrationally independent system is an approximation, it does make it possible to utilize procedures commonly used in discussions of the spectrum of liquids and gases. Results of this treatment provide stronger support for and a more detailed picture of the structure of the adsorbed species than a more primitive interpretation of the spectrum. Accordingly, we feel the approximation is a valuable one which may be applied cautiously with profit to infrared studies of adsorbed species.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The authors also acknowledge the benefit of many helpful discussions of this work with Professor D. W. Robinson.

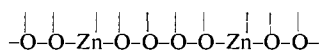
The Nature of Adsorbed Propylene on Zinc Oxide. II. Reactions of π -Allyl Species

A. L. Dent and R. J. Kokes*

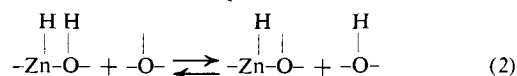
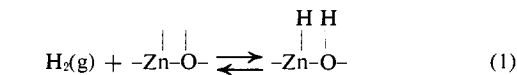
Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. Received April 27, 1970

Abstract: The reaction over zinc oxide of propylenes (labeled and unlabeled) in the presence and absence of deuterium has been studied both by traditional mechanistic and infrared techniques. Isomerization of labeled propylene (intramolecular hydrogen exchange) and intermolecular hydrogen exchange occur at roughly comparable rates. Furthermore, propylene-deuterium exchange occurs at a rate competitive with the addition reaction and the product contains a distribution of deuteriopropenes. Comparison of these results with those obtained for ethylene leads to the conclusion that those reactions that occur only with propylene are a consequence of the formation of reactive π -allyl species.

Hydrogenation of ethylene over zinc oxide has been the subject of several recent papers from this laboratory.¹⁻⁴ These studies led to the conclusion that hydrogen adsorption and reaction occur on isolated, independent, active sites consisting of adjacent zinc and oxygen ions. It was suggested that these sites arise from surface reconstruction in which zinc ions systematically fill the trigonal holes in a surface layer of oxide ions defining a close-packed array. Schematically, we can picture this surface as follows



wherein the neighboring zinc and oxygen atoms represent active sites. The *principal* steps in the suggested mechanism are



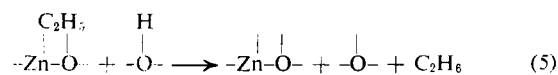
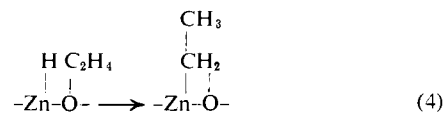
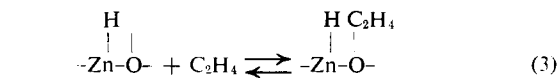
* Address correspondence to this author.

(1) W. C. Conner, R. A. Innes, and R. J. Kokes, *J. Amer. Chem. Soc.*, **90**, 6858 (1968).

(2) W. C. Conner and R. J. Kokes, *J. Phys. Chem.*, **73**, 2436 (1969).

(3) A. L. Dent and R. J. Kokes, *ibid.*, **73**, 3772, 3781 (1969).

(4) A. L. Dent and R. J. Kokes, *J. Amer. Chem. Soc.*, **91** 7207 (1969).



where $\begin{array}{c} | \\ -Zn-O- \end{array}$ represents the active site and $\begin{array}{c} | \\ -O- \end{array}$ a surface oxygen atom between sites. The basis for this scheme has been discussed elsewhere.³ Salient features pertinent to the current work are: (a) infrared studies are consistent with this scheme insofar as they suggest that ethylene chemisorbs (weakly) without dissociation and with the double bond intact to form a weak " π complex";⁵ (b) because of the nature of adsorbed ethylene and the irreversibility of steps 4 and 5, addition of deuterium to ethylene leads cleanly to $C_2H_4D_2$;¹ (c) step 2 in the above scheme, which provides for site-to-site hydrogen migration, is required to explain the observed H_2 - D_2 exchange.²

(5) A. L. Dent and R. J. Kokes, unpublished results.