JOURNAL OF CATALYSIS **61**, 503–514 (1980)

Infrared and Raman Spectroscopic Study of Some Aromatic Acetylenic Compounds Adsorbed on Zinc Oxide

T. T. NGUYEN,*,[1] J. C. LAVALLEY,† J. SAUSSEY,† AND N. SHEPPARD*

**School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, England, and*
†Laboratoire de Spectrochimie, U.E.R. de Sciences, Université de Caen,
14032 Caen Cedex, France

Received January 22, 1979

Infrared and Raman spectra from 3-phenyl-1-propyne ($C_6H_5CH_2C{\equiv}CH$) and 1-phenyl-1-propyne ($C_6H_5C{\equiv}CCH_3$) adsorbed on zinc oxide are reported. Isomerization between these adsorbates occurs via the formation of phenylallene, the third isomeric compound ($C_6H_5CH{=}C{=}CH_2$). Both adsorbates have a common behavior over zinc oxide in that each gives rise to two types of dissociative chemisorption to yield acetylide species and propargyllic species; the former results from dissociation of the acetylenic hydrogen and the latter from removal of a proton attached to a carbon atom in an α-position to the triple bond. The propargyllic species are considered to be intermediates in the isomerization reactions, and their two possible structures $[C_6H_5CH{\overset{...}{-}}C{\overset{...}{=}}CH]^-$ and $[C_6H_5{-}C{\overset{...}{=}}C{\overset{...}{-}}CH_2]^-$ are characterized by intense infrared absorptions identically positioned at 1862 cm^{-1} which are assignable to the $\nu(C{\overset{...}{=}}C)$ modes. The acetylide species $C_6H_5CH_2C{\equiv}C\ldots Zn$(surface) are characterized by the $\nu(C{\equiv}C)$ bands in the region 2080 to 2110 cm^{-1} in both infrared and Raman spectra. Infrared spectra from $C_6H_5CD_2C{\equiv}CD$ adsorbed on ZnO pretreated with D_2O were also recorded to help to assign the infrared bands of propargyllic species from adsorbed non-deuterated compounds. They provide evidence for the two types of propargyllic species $[C_6H_5CD{\overset{...}{-}}C{\overset{...}{=}}CD]^-$ and $[C_6H_5C{\overset{...}{=}}C{\overset{...}{-}}CD_2]^-$ in the form of absorption bands at 1830 and and 1857 cm^{-1}, respectively.

INTRODUCTION

A number of infrared studies have suggested that zinc oxide can function as a base in heterogeneous catalytic reactions (*1–3*). For example, the chemisorption of propylene on ZnO has been shown by Dent and Kokes (*4*) to be dissociative and involves the rupture of a methyl carbon–hydrogen bond; the hydrogen thus removed combines with an oxide ion from the surface to form an OH^- species while the remaining hydrocarbon moiety, considered to interact with a zinc ion, was demonstrated to be a symmetrical species of the formula (CH_2CHCH_2). More recently Nguyen and Sheppard shown that the allyl species is anionic in nature (*5*), and, as in a previous paper on the infrared spectra of such species (*6*), we have assumed the adsorbed species from the acetylenes to be also negatively charged.

When methylacetylene is adsorbed on zinc oxide (*7*), dissociation again occurs to yield two distinct types of chemisorbed species: a methylacetylide species and a propargyllic species. The former results from the removal of the acetylenic hydro-

---

[1] Present address: Department of Chemical Engineering, University of Adelaide, P. O. Box 498, Adelaide, SA 5001, Australia.

0021-9517/80/020503-12$02.00/0

gen whereas the latter is formed via the dissociation of one of the methyl CH bonds. Chang and Kokes (*7*) considered that the acetylide species exists only to a limited extent but that the propargyllic species is the principal one formed from chemisorbed methylacetylene. The propargyllic species was also observed by the same authors (*7*) in the spectrum from chemisorbed allene and was thus considered as an intermediate in the methylacetylene/allene isomerization over zinc oxide. The propargyllic species can be represented by two forms contributing to a resonance hybrid:

$$\bar{\mathrm{C}}\mathrm{H_2}\text{—}\mathrm{C}\equiv\mathrm{CH} \leftrightarrow \mathrm{CH_2}=\mathrm{C}=\bar{\mathrm{C}}\mathrm{H} \text{ or } [\mathrm{CH_2}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{=}\mathrm{CH}]^-.$$

A feature common to both the reaction of propylene and of methylacetylene over zinc oxide is that the respective allyl or propargyllic species acts as an intermediate in a 1,3-hydrogen transfer reaction across the unsaturated carbon skeleton.

More recently, new infrared data (*6*) obtained from a number of substituted acetylenes and isomeric allenes chemisorbed on ZnO have led to a substantial reinterpretation of previous spectroscopic results from methylacetylene. As a result Saussey *et al.* (*6*) have emphasized the greater number of infrared bands due to the acetylide species ($\mathrm{CH_3}\text{—}\mathrm{C}\equiv\bar{\mathrm{C}}$) which coexists with the propargyllic species. These authors also studied the isomeric molecules 1-butyne, 2-butyne, and 1,2-butadiene (*6*). Similar types of infrared spectra were obtained from these three starting compounds following adsorption on ZnO, and it was suggested (*6*, *8*) that isomerization between these various structures occurs via the formation of the following intermediate propargyllic species

$$[\mathrm{CH_3}\text{—}\mathrm{C}\overset{\cdots}{=}\mathrm{C}\overset{\cdots}{-}\mathrm{CH_2}]^- \quad [\mathrm{CH}\overset{\cdots}{=}\mathrm{C}\overset{\cdots}{-}\mathrm{CH}\text{—}\mathrm{CH_3}]^-.$$

Infrared studies of chemisorbed species from 1-butyne on ZnO selectively poisoned by CO_2, HCOOH, NH_3, or C_5H_5N have given evidence for two types of adsorption sites: Lewis acid–base sites $Zn^{2+}O^{2-}$ which are the catalytic sites in the isomerization process, and other sites which might be interstitial zinc atoms or ions (*8*, *9*). Gravimetric measurements have shown that these two types of sites are independent (*8*, *9*).

Raman spectroscopy has been demonstrated to constitute a valuable tool in the studies of surface adsorbed species (*10*, *11*). In most of these studies, in order to obtain good spectral sensitivity, the solid adsorbents employed have been of the silica, alumina, and zeolite types which have very high surface areas (several hundred $m^2\ g^{-1}$) and have usually been white. The adsorbates chosen have also mainly been strong Raman scatterers. For example, good-quality Raman spectra have been reported of acetylene (*12*) and pyridine (*13*) adsorbed on cation-exchanged zeolites. Zinc oxide as normally obtainable has a much less favorable surface area (less than 10 $m^2\ g^{-1}$) than that of the oxides mentioned above and no Raman studies of adsorption on this heavy metal oxide have been reported earlier. Recently, Nguyen and Sheppard have initiated Raman work on molecules chemisorbed on ZnO with a study of the adsorption of propylene (*5*).

The present work forms part of our continued studies of this catalyst. We report herein infrared and Raman spectra obtained from the chemisorption of 3-phenyl-1-propyne and 1-phenyl-1-propyne on ZnO. Analogous to the behavior of methylacetylene, 1-butyne, and 2-butyne mentioned above, these two isomeric compounds should constitute interesting adsorbates to yield acetylide species and propargyllic species on ZnO. In spectroscopic terms, the adsorbates above are favorable choices for Raman studies because both the phenyl moiety and the acetylenic moiety are strong Raman scatterers. A combined use of both Raman and infrared techniques which are complementary to each other should prove to be very helpful in examining the structures of various chemisorbed species from the adsorbates mentioned above.

EXPERIMENTAL

Materials. The zinc oxide powder used was Kadox 15 from the New Jersey Zinc Co.; its surface area was reported (*14*) to be 8.40 m^2 g^{-1}. The oxygen used in the pretreatment of ZnO was obtained from BDH with a stated purity of 99.6%. The 1-phenyl-1-propyne was obtained from the Aldrich Chemical Co. It was redistilled before use. 3-Phenyl-1-propyne was obtained from 1-phenyl-1-propyne treated with *n*-butyllithium in ether (*15*). 3-Phenyl-1-propyne (D_3-1,3,3) was obtained in a similar way, using deuterium oxide as hydrolysis agent (*15*). The ^{13}C NMR spectrum of the product showed that the isotopic purity of the methylene and the acetylenic $C{\equiv}CD$ groups were about 95%. On standing the 3-phenyl-1-propyne samples turned a pale yellow color, and they were therefore redistilled immediately before use.

Pretreatment of the oxide sample. The white zinc oxide powder of area ca. 8 m^2 g^{-1} (Kadox 15 from the New Jersey Zinc Co.) was pressed into the form of discs at a pressure of 1000 kg cm^{-2}. Their diameter and weight were 16 mm and ca. 0.5 g for infrared experiments, and 25 mm and ca. 1 g for Raman studies. The discs were pretreated in greaseless *in situ* infrared or Raman cells. The zinc oxide samples were degassed at 25°C at 5×10^{-6} Torr for several hours. Then 16 Torr of very dry oxygen was introduced and the sample was progressively heated to 450°C. It was maintained at this temperature for 2 to 5 hr with regular replacement of oxygen so as to remove any desorbed water. After cooling in oxygen to 250°C the disc was then evacuated at 5×10^{-6} Torr for 30 min to 1 hr prior to introduction of an adsorbate. This type of activation led to a coverage of 3.2×10^{-5} mol g^{-1} of 1-butyne.

Recording spectra. Infrared spectra were recorded on a Perkin-Elmer 580 at Caen or a Digilab FTS 14 Fourier transform interferometer with spectral ratioing facilities at Norwich.

Raman spectra were recorded on a Spex 1401 double monochromator coupled to a Coherent Radiation mixed gas argon and krypton ion laser. The exciting line at 568.2 nm was used and isolated from interfering plasma emission by an Anaspec 300 S monochromator. The choice of the yellow exciting line at 568.2 nm over the blue (488 nm) and the red (647.1 nm) lines was dictated by a compromise between minimizing fluorescence in the Raman spectra from the adsorbed species and obtaining reasonable sensitivity from the detection system. The silica cell containing the disc sample was positioned at 45° relative to the incident laser beam. Right-angle viewing optics were employed. Since the power of the focussed laser beam incident on the sample was about 15 to 20 mW, in order to allow sufficient energy to reach the detector a spectral slitwidth of 10 cm^{-1} was used in adsorption experiments.

Infrared and Raman spectra of the liquid adsorbates were also recorded. In the latter case, a spectral slitwidth of 4 cm^{-1} was used.

RESULTS

3-Phenyl-1-propynes ($C_6H_5CH_2C{\equiv}CH$ *and* $C_6H_5CD_2C{\equiv}CD$)

The infrared spectrum of the liquid $C_6H_5CH_2C{\equiv}CH$ shows strongest bands at 630 and 3298 cm^{-1} attributed to the $\delta({\equiv}CH)$ and $\nu({\equiv}CH)$ modes, respectively. In the CH stretching region bands at 2920, 2895, and 2820 cm^{-1} are assigned to $\nu_{as}(CH_2)$, $\nu_s(CH_2)$, and $2\delta(CH_2)$ whereas other bands at 3105, 3085, 3061, and 3030 cm^{-1} arise from the $\nu(CH)$ of the phenyl ring. The $\nu(C{\equiv}C)$ mode appears as a weak

TABLE 1

Infrared Spectra (cm^{-1}) from 3-Phenyl-1-propynes Adsorbed on ZnO[a]

3-Phenyl-1-propyne		3-Phenyl-1-propyne (D_3-1,3,3)	
Liquid	Adsorbed on ZnO	Liquid	Adsorbed on ZnO[b]
1029 m		1021 m, 1037 w	
1075 m	1070 vw	1090 w, 1070 w	1070 w
1167 w	1153 vw	1160 bd	1155 vw
1175 sh	1175 vw	1180 vw	1180 vw
1204 w			
		1228 w, 1213 w	1215 ?
1263 bd	1260 vw		
1287 m	1288 vw	1278 w	1270 vw
1336 w, 1325 w		1312 w	
1420 s	1420 w		1413 ?
1454 vs	1453 vs	1449 vs	1450 m
1495 vs	1492 vs	1495 vs	1495 vs
	1508 ?		1510 ?
1584 sh	1570 ?	1584 w	1572 ?
1598 m	1595 s	1602 m	1593 m
			1830 vs
	1862 vs		1857 m
	1942 (w)		≃1940 vw
1950 vw		1950 vw	
		1983 w	
		2068 vw, 2050 vw	
	2075 bd, w		2075 bd, w
		2110 w	
2120 w	2110 w		2120 sh
			2165 w
		2195 vw	
			2250 w
		2592 vs	≃2500 bd, s
2820 vw	2830 vw		2602 m
2895 m	2890 sh		
2920 w	2920 bd, w		
3010 sh	2950 ?		
3030 m	3030 m	3028 m	3030 m
3061 m	3065 m	3060 m	3065 m
3085 w	3083 w	3083 w	3085 w
3105 sh	≃3105 sh	3108 vw	3108 vw
3298 vs			
	3350 bd, s		
	3525 bd, m		

[a] sh, shoulder; vw, very weak; w, weak; m, medium; s, strong; vs, very strong; bd, broad.

[b] The zinc oxide has been pretreated with D_2O.

absorption at 2120 cm^{-1}. Stronger absorptions at 1420 and at 1263 cm^{-1} are attributed to $\delta(CH_2)$ and $2\delta(\equiv CH)$, respectively. Other strong bands at 1598, 1495, and 1454 cm^{-1} are characteristic of phenyl ring ν(C—C) vibrations (*16*). The overtone $2\delta(\equiv CH)$ is well known to be a strong one.

The infrared spectrum of the liquid $C_6H_5CD_2C\equiv CD$ shows bands at 2592, 1983, and near 1000 cm^{-1} due to the

$\nu(\equiv\text{CD})$, $\nu(\text{C}\equiv\text{C})$, and $2\delta(\equiv\text{CD})$, respectively. A weak absorption at 2195 cm^{-1} is assigned to $\nu_{as}(\text{CD}_2)$ whereas other weak bands at 2110, 2068, and 2050 cm^{-1} could arise from $\nu_s(\text{CD}_2)$ in interaction with overtones or combinations, for example $2\delta(\text{CD}_2) = 2 \times 1037$ cm^{-1}. The infrared spectra of both compounds are summarized in Table 1.

The Raman spectrum of the liquid 3-phenyl-1-propyne $\text{C}_6\text{H}_5\text{CH}_2\text{C}\equiv\text{CH}$ in general agrees with its infrared spectrum. A most intense line at 1008 cm^{-1} is attributed to the phenyl ring breathing mode while a strong band at 1605 cm^{-1} is assigned to another $\nu(\text{C}=\text{C})$ mode of the aromatic ring. The $\nu(\text{C}\equiv\text{C})$ mode appears as a strong single band at 2125 cm^{-1} which has been considered (*17*) to be characteristic in Raman spectra of acetylenic compounds containing the propargyl end group $-\text{CH}_2\text{C}\equiv\text{CH}$. In the $\nu(\text{CH})$ region two asymmetrical features of medium, comparable intensity at 2900 and 3063 cm^{-1} are assigned to the $\nu_s(\text{CH}_2)$, and the $\nu(\text{CH})$ of the phenyl ring, respectively. A very weak band near 3300 cm^{-1} is attributed to the acetylenic $\nu(\text{CH})$ mode. The wavenumbers are listed Table 2.

Infrared spectra of adsorbed species. The infrared spectrum of $\text{C}_6\text{H}_5\text{CH}_2\text{C}\equiv\text{CH}$

TABLE 2

Raman Spectra[a] ($\Delta\bar{\nu}$/cm^{-1}) from 3-Phenyl-1-propyne Adsorbed on ZnO

3-Phenyl-1-propyne (liquid) ($\text{C}_6\text{H}_5-\text{CH}_2-\text{C}\equiv\text{CH}$)	Adsorbed species on ZnO	Phenylallene[b] (liquid) ($\text{C}_6\text{H}_5-\text{CH}=\text{C}=\text{CH}_2$)
995 (5.0)		
1008 (178.0)	1002 (12.6)	1001 vs[d]
1032 (40.0)	*c*	
1160 (5.0)		1178 s[d]
1190 (15.0)	≃1200 (shoulder)	1196 s
1207 (5.0)		
	1290 (2.6)	1287 s
	1350 (2.2)	1347 s
1425 (2.5)		
1590 (5.0)	1500 (1.0)	1496 s
1605 (10.0)	1605 (10.0)	1600 s
	1950 (2.0)	1944 vs
2125 (60.0)	2110 (0.4)	
2830 (2.5)		
2900 (16.3)		
2928 (6.3)		
2986 (2.5)	2990 (2.2)	2982 s
3011 (2.5)		
3048 (shoulder)		
3063 (30)	3068[e]	3057 s
3072 (shoulder)		
3305 (2.5)		

[a] Arbitrary relative peak intensity in parentheses.

[b] See Ref. (*20*). Only the stronger Raman bands are cited here.

[c] The spectral region from 980 to 1240 cm^{-1} is badly complicated by strong features from the ZnO adsorbent.

[d] s, strong; vs, very strong.

[e] This region is often complicated by problems of localized fluorescence and possibly interfering plasma lines.

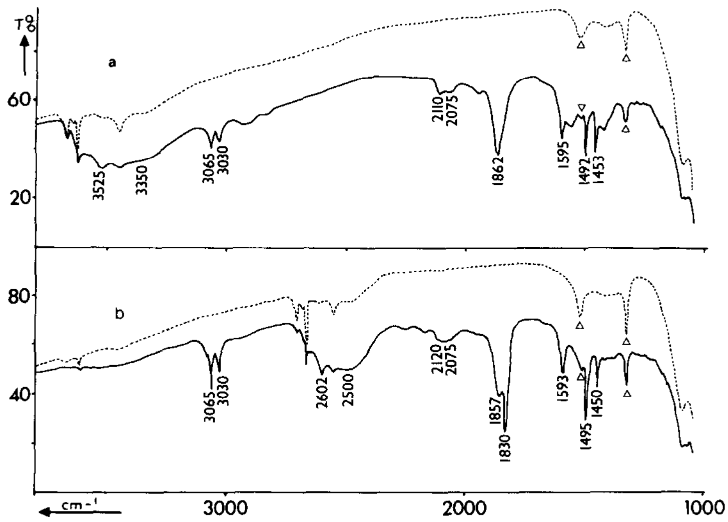

FIG. 1. Infrared spectra of 3-phenyl-1-propynes adsorbed on zinc oxide. (a) ZnO spectrum prior to adsorption (broken line) and spectrum of $\simeq$0.5 Torr of $C_6H_5CH_2C{\equiv}CH$ adsorbed on ZnO (solid line). (b) ZnO spectrum prior to adsorption (the hydroxyl groups have been exchanged with heavy water) (broken line) and spectrum of $\simeq$0.5 Torr of $C_6H_5CD_2C{\equiv}CD$ adsorbed on this sample.

chemisorbed on ZnO is shown in Fig. 1. In the 3300 to 3700 cm^{-1} range, it is apparent that the intensity of the background stretching OH band at 3670 cm^{-1} decreased substantially upon adsorption while new bands appeared near 3350 and 3525 cm^{-1}, the former being considerably broader than the latter. By analogy with earlier results from adsorbed propynes and butynes (*6*), we assign the 3350 cm^{-1} band to the stretching vibration of OH groups arising from the formation of acetylide species, and the 3525 cm^{-1} band to OH groups resulting from the formation of propargyllic species (see later). The latter band is probably also due to hydrogen-bonded species involving the surface OH group and the aromatic ring. Evidence for this comes from the observation of substantial removal of the background OH band at 3670 cm^{-1} in spectra obtained after ratioing against ZnO background. This is confirmed by the infrared spectra from adsorbed benzene —(D_0) and —(D_6) and adsorbed ethynyl benzene which show the formation of hydrogen-bonded species occurs displacing the background OH band to 3525 and 3510 cm^{-1}, respectively (*18*). Spectra ratioed against ZnO background also indicate a slight intensity decrease of the background OH band at 3620 cm^{-1}. This probably suggests that these OH groups are also involved, to a lesser extent, in hydrogen bonding interaction. However, a more detailed analysis is difficult because of the considerably intense and broad profile of the spectrum in this region. In the spectrum of $C_6H_5CD_2C{\equiv}CD$ adsorbed on zinc oxide pretreated with D_2O, new OD bands now appeared at 2602 and near 2500 cm^{-1} (see Fig. 1), corresponding to their 3525 and 3350 cm^{-1} hydroxyl counterparts. In this case, the intensity of the background OD band at 2709 cm^{-1} was found to decrease considerably upon adsorption.

In the 1800 to 2000 cm^{-1} range, the spectrum from adsorbed $C_6H_5CH_2C{\equiv}CH$ shows four absorptions of interest at 1862, 1942, 2075, and 2110 cm^{-1}. The latter two weak bands are assigned to the $\nu(C{\equiv}C)$ mode of the chemisorbed acetylide species $C_6H_5CH_2C{\equiv}C\ldots Zn$(surface). This is in agreement with previous results (*6*) from propynes and butynes adsorbed on ZnO. Saussey and Lavalley (*9*) have shown that two types of adsorption sites can be involved in the formation of acetylide species leading to two kinds of species with slightly different $\nu(C\equiv C)$ wavenumbers. As expected, these $\nu(C\equiv C)$ bands were not affected by the isotopic H → D substitution: they appeared too in the spectrum from adsorbed $C_6H_5CD_2C\equiv CD$[2] (see Fig. 1 and Table 1). The weak band at 1942 cm^{-1} is assigned to the $\nu_{as}(C{=}C{=}C)$ mode of phenylallene formed from the isomerization of the starting compound $C_6H_5CH_2C\equiv CH$ (see the Raman spectra later). Contrary to the case of adsorbed butynes (*6*), only one fairly broad band at 1862 cm^{-1} is assignable to the $\nu(C\overset{\cdots}{=}C)$ mode of propargyllic species whereas two forms of these intermediate species would be expected, namely $[C_6H_5CH\overset{\cdots}{-}C\overset{\cdots}{=}CH]^-$ and $[C_6H_5C\overset{\cdots}{=}C\overset{\cdots}{-}CH_2]^-$. On the other hand, the spectrum from adsorbed $C_6H_5CD_2C\equiv CD$ contains two strong absorptions at 1830 and 1857 cm^{-1} assignable to these two forms of propargyllic species. These spectral features will be discussed later.

For both the undeuterated and deuterated adsorbates, the $\nu(CH)$ wavenumbers of the phenyl ring were not affected by their adsorption on ZnO. However, we note that the intensity of the 3030 cm^{-1} band is slightly stronger than that of the 3060 cm^{-1} band in the liquid spectra whereas it is the reverse in the adsorbed phase. By analogy with earlier results (*6*, *9*), $\nu(CH)$ bands in the region from 2800 to 3000 cm^{-1} can be assigned to $\nu(CH_2)$ modes of the chemisorbed acetylide species. In the region 1600 to 1000 cm^{-1}, no remarkable changes from liquid spectra occurred.

When the sample containing adsorbed species from $C_6H_5CH_2C\equiv CH$ was allowed to stand for a sufficiently long period of time (using the dispersive Perkin Elmer instrument) or, alternatively, when it was subjected to mild heating at 80°C (using the Digilab interferometer) the intensity of the band at 1942 cm^{-1} assigned to physically adsorbed phenylallene was observed to decrease while two new weak bands developed at 2250 and 2210 cm^{-1}. The latter two bands are characteristic in the spectrum of liquid 1-phenyl-1-propyne and indicate further transformation of phenylallene to the former isomeric compound (see later).

Raman spectra of adsorbed species. The Raman spectrum from the chemisorbed species in the region above 800 cm^{-1} and the spectrum of the liquid adsorbate are shown in Figs. 2a and b. The strongest bands arising from the adsorbed species were now observed at 1002 and 1605 cm^{-1} together with other weaker bands at 1290, 1350, 1500, 1950, 2990, and 3068 cm^{-1}. A very intense, broad and asymmetrical feature attributed (*19*) to multiphonon processes in ZnO interferes in the region from 940 to 1240 cm^{-1}. However, the presence of a shoulder near 1200 cm^{-1} is still detected on the high frequency side of this feature. Also, a very weak band due to the $\nu(C\equiv C)$ mode was noticed near 2110 cm^{-1}. This band was shifted by about 15 cm^{-1} from the $\nu(C\equiv C)$ mode in the liquid spectrum and was remarkably different in intensity from the latter. It is attributed to an acetylide species, in agreement with the infrared results. The Raman experimental conditions used probably preclude detection of the overlapping band near 2075 cm^{-1} as observed in the infrared.

The Raman spectrum obtained following adsorption of 3-phenyl-1-propyne on ZnO is, with the exception of the band near 2110 cm^{-1}, in fact very closely similar to the strongest bands in the Raman spectrum reported for the isomeric liquid phenylallene (*20*). The band at 1950 cm^{-1} is attributed to the $\nu_{as}(C{=}C{=}C)$ mode of the

---

[2] The other bands in the 2300–2000 cm^{-1} region are related to the $\nu(CD_2)$ modes of the acetylide species.

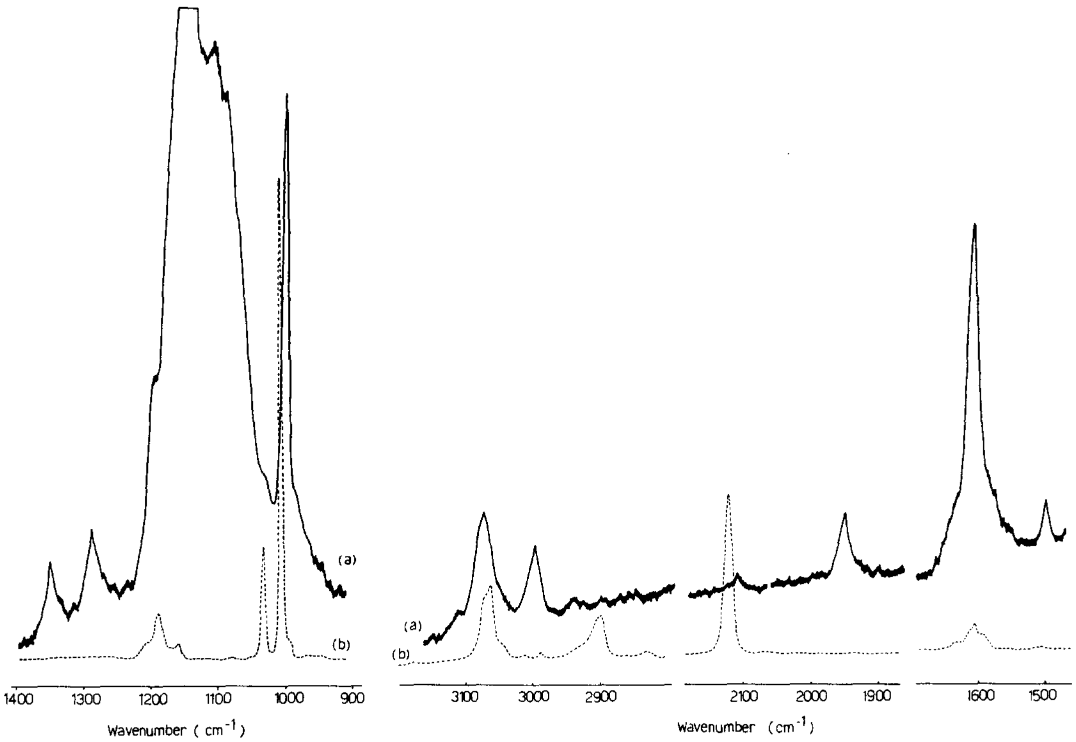

FIG. 2. (a) Raman spectra of 3-phenyl-1-propyne in the region 900 to 1400 cm^{-1}. Spectrum of the liquid (broken line) and of adsorbed species on zinc oxide (solid line). (b) Raman spectra of 3-phenyl-1-propyne in the region above 1500 cm^{-1}. Spectrum of the liquid (broken line) and of adsorbed species on zinc oxide (solid line).

allene, and is present also in the infrared spectrum described earlier. The strong band at 2990 cm^{-1} is readily assigned to the symmetric $\nu(CH_2{=})$ mode of phenylallene; this band is characteristic for both its position and intensity in Raman spectra of a number of allenic compounds (*20, 21*). The symmetrical $\nu(C{=}C{=}C)$ mode of phenylallene was reported (*20*) to be at 1080 cm^{-1}. However, detection of this band from the adsorbed species would be very difficult because this spectral region is badly complicated by strong features from the ZnO adsorbent. The Raman results from the adsorbed species together with those from the liquid adsorbate 3-phenyl-1-propyne and from phenylallene are summarized in Table 2.

1-Phenyl-1-propyne ($C_6H_5C{\equiv}CCH_3$)

The infrared spectrum of the liquid $C_6H_5C{\equiv}CCH_3$ shows two absorptions of medium intensity at 2216 and 2249 cm^{-1} assigned to the $\nu(C{\equiv}C)$mode in interaction with an overtone or a combination band (*22, 23*). The $\nu(CH)$ bands of the phenyl ring and other bands in the 1000 to 1700 cm^{-1} region such as the stronger ones at 1598, 1490, 1442, 1070, and 1032 cm^{-1} are similar to those observed in the infrared spectrum of ethynylbenzene (*14*). Fundamentals due to the methyl group lie at 2957 (ν_{as}), 2916 (ν_s), 1440 (δ_{as}), and 1378 cm^{-1} (δ_s). The Raman spectrum of the liquid contains two strong bands, as expected, at 2222 and 2256 cm^{-1} arising from the $\nu(C{\equiv}C)$ mode. Other intense bands at 1005, 1604, and 3068 cm^{-1} are, as in the case of 3-phenyl-1-propyne, again assigned to vibrations associated with the phenyl ring whereas another strong band at 1268 cm^{-1} is attributed to a vibration considerably localised in the bond between the phenyl ring and the lateral acetylenic chain.

The unusually strong intensity of the latter has been related (*22*) to the conjugation effect resulting from the direct substitution of the phenyl ring by the acetylenic bond. The other strong bands at 974 and 2920 cm^{-1} are assigned to the $\nu(\equiv C-C)$ mode and the $\nu_s(CH_3)$ of the methyl group, respectively.

Infrared spectra of adsorbed species. The infrared spectra from adsorbed 1-phenyl-1-propyne is in general quite similar to that from adsorbed 3-phenyl-1-propyne already described in the foregoing section. Again in the region 1800 to 1900 cm^{-1} there is only one absorption of rather strong intensity situated at 1862 cm^{-1}. This band is attributed to the intermediate propargyllic species. The band at 1942 cm^{-1} assignable to the $\nu_{as}(C=C=C)$ of phenylallene was noted to be much weaker than before. In the $\nu(C\equiv C)$ region, in addition to two very weak absorptions near 2215 and 2250 cm^{-1}, there appeared again two stronger overlapping bands near 2110 and 2080 cm^{-1} which are attributed to the chemisorbed acetylide species (see discussion later).

Raman spectra of adsorbed species. The Raman spectrum of the adsorbed species shows a number of strong bands at 972, 1006, 1265, 1604, 2216, 2254, 2929, and 3070 cm^{-1} which are closely similar in positions to their counterparts in the liquid spectrum of the adsorbate. However, in the $\nu(C\equiv C)$ region a new weak band was noticed at 2107 cm^{-1} with a relative peak intensity of about one-fifth of that of the more intense band at 2254 cm^{-1} (see Fig. 3). Again the band at 2107 cm^{-1} is attributed to the acetylide species, in agreement with the Raman results from adsorbed 3-phenyl-1-propyne. The band at 2254 cm^{-1} and its companion band at 2216 cm^{-1} are considered to arise from a strongly held physically adsorbed species which is similar to the adsorbate molecule since their peak intensity ratio is almost identical to that in the liquid spectrum. These bands were found to regrow after the sample had been allowed to stand at room temperature (but unexposed to the laser beam) for a sufficiently long period of time. The spectra are shown in Fig. 3. Parallel infrared experiments indicated that the physically adsorbed species was hydrogen-bonded to the OH groups of the zinc oxide surface, and its reformation was likely to result from readsorption of some of the adsorbate molecules trapped from the neoprene O-ring of the cell during evacuation. The Raman spectra of the adsorbed species together with that of the liquid adsorbate 1-phenyl-1-propyne are summarized in Table 3.

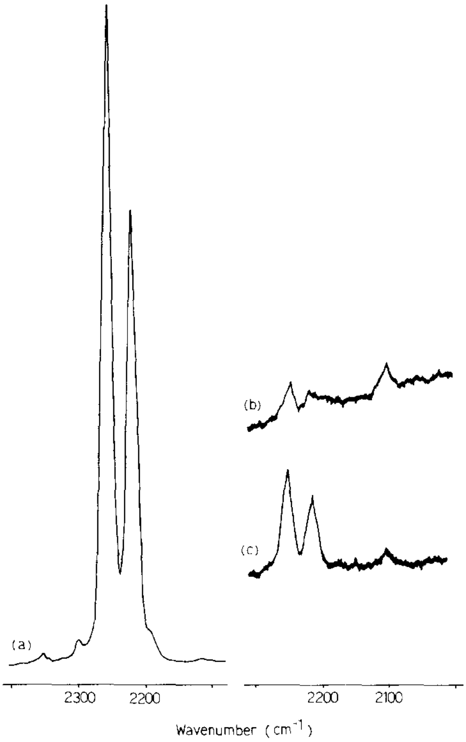

FIG. 3. Raman spectra of 1-phenyl-1-propyne in the region 2000 to 2400 cm^{-1}. (a) Liquid; (b) adsorbed species on zinc oxide immediately after second evacuation; and (c) repeated spectrum after (b).

DISCUSSION

The combined infrared and Raman results clearly give evidence that 3-phenyl-1-propyne isomerizes to phenylallene over zinc oxide. When 1-phenyl-1-propyne is

TABLE 3

Raman Spectra[a] ($\Delta\tilde{\nu}/\mathrm{cm}^{-1}$) from 1-Phenyl-1-propyne Adsorbed on ZnO

Liquid[b]	Adsorbed on ZnO			
	After first evacuation		After second evacuation	
	Immediate scan	Repeated scan	Immediate scan	Repeated scan
974 (8.2)	972 (7.7)	973 (8.0)	972 (5.7)	972 (7.1)
1005 (10.8)	1006 (11.0)	1006 (11.0)	1004 (14.3)	1005 (10.0)
1033 (1.2)				
1060 (0.2)				
1160 (1.2)	[c]	[c]	[c]	[c]
1180 (1.8)				
1250 (0.7)				
1268 (9.5)	1265 (7.3)	1268 (7.8)	1268 (4.3)	1265 (6.7)
1288 (0.7)				
1333 (0.1)				
1383 (1.2)		1387 (0.8)		
1446 (0.4)				
1494 (1.2)		1494 (0.8)		
1577 (0.4)				
1604 (10.0)	1604 (10.0)	1604 (10.0)	1602 (10.0)	1604 (10.0)
	2107 (1.9)	2106 (1.0)	2106 (5.7)	2106 (0.9)
2192 (0.4)				
2222 (4.9)	2216 (6.5)	2218 (5.2)	2215 (4.3)	2216 (4.8)
2256 (7.3)	2254 (10.0)	2255 (7.8)	2252 (7.1)	2252 (7.1)
2355 (0.1)				
2857 (0.2)	2872 (0.7)	2868 (0.6)		
2920 (3.3)	2929 (5.0)	2929 (4.2)	2928 (2.9)	2927 (3.3)
2957 (0.1)				
2980 (0.1)				
3068 (2.3)	3070[d]	3070	3070	3068

[a] Arbitrary relative peak intensity in parentheses.

[b] See Refs. (*20–22*) for detailed assignments.

[c] The region from 940 to 1240 cm^{-1} is badly interfered by strong features from the adsorbent ZnO.

[d] See footnote *d* in Table 2.

used as the starting compound, isomerization to phenylallene also occurs as indicated by the infrared spectrum. The isomerization reactions most probably take place via the formation of the intermediate propargyllic species which would be expected to have the following types of structures.

$$[\mathrm{C_6H_5{-}CH\overset{\cdots}{=}C\overset{\cdots}{\equiv}CH}]^- \qquad \mathrm{(I)}$$

and

$$[\mathrm{C_6H_5{-}C\overset{\cdots}{\equiv}C\overset{\cdots}{=}CH_2}]^-. \qquad \mathrm{(II)}$$

Either starting with the adsorbate 3-phenyl-1-propyne or 1-phenyl-1-propyne there forms only one intense absorption of some breadth at the same wavenumber of 1862 cm^{-1} assignable to the $\nu(\mathrm{C\overset{\cdots}{\equiv}C})$ mode of the propargyllic species. It thus appears that the two slightly structurally different propargyllic species above give rise to one overlapping absorption at the same position in the infrared spectrum. This is not at all surprising. 1-Butynes adsorbed on ZnO have been found to give rise initially to an infrared band near 1860 cm^{-1} (*6*). This suggests that propargyllic species of structure (I), a mono-substituted type, are formed following the adsorption of 3-phenyl-1-propyne. When $C_6H_5C{\equiv}CCH_3$ is adsorbed, the first intermediate would be expected to be of type (II), i.e., a di-substituted species. Earlier, the adsorption of 2-butynes has been found (*6*) to give rise initially to the formation of di-substituted propargyllic species which tend to have the $\nu(C\overset{\cdots}{=}C)$ mode at higher wavenumbers, by about 20 cm^{-1}, than their mono-substituted counterparts. We interpret the rather low $\nu(C\overset{\cdots}{=}C)$ wavenumber observed for the species $[C_6H_5{-}C\overset{\cdots}{=}C{-}CH_2]^-$ as reflecting the conjugation effects in this structure.

When the deuterated compound $C_6H_5CD_2C{\equiv}CD$ is adsorbed on zinc oxide pretreated with D_2O the observation of two absorptions at 1830 and 1857 cm^{-1} is also interesting. The latter band is strong enough to argue against the possibility of isotopic impurities (for example, $C_6H_5CD_2C{\equiv}CH$ or nonexchanged OH groups) leading to such impurities (for example, $C_6H_5CD_2C{\equiv}CH$ or nonexchanged OH groups) leading to such species as $[C_6H_5{-}CD\overset{\cdots}{=}C\overset{\cdots}{=}CH]^-$ which could have a $\nu(C\overset{\cdots}{=}C)$ band at 1857 cm^{-1}. Since mono-substituted propargyllic species have been found (*6*) to be sensitive to the isotopic $\equiv CH \rightarrow \equiv CD$ substitution, we attribute the 1830 cm^{-1} band to the species $[C_6H_5{-}CD\overset{\cdots}{=}C\overset{\cdots}{=}CD]^-$. This attribution gives support to the assignment of the 1860 cm^{-1} band to the species $[C_6H_5{-}CH\overset{\cdots}{=}C\overset{\cdots}{=}CH]^-$ mentioned above. The other band at 1857 cm^{-1} resulting from the deuterated adsorbate is attributed to the di-substituted species $[C_6H_5{-}C\overset{\cdots}{=}C\overset{\cdots}{=}CD_2]^-$ since the $\nu(C\overset{\cdots}{=}C)$ mode of this type of species has been found (*6*) to be insensitive to the isotopic substitution. In contrast to the infrared results, no Raman spectra are observable from the intermediate propargyllic species.

Phenylallene formed from the isomerization of 3-phenyl-1-propyne also isomerizes itself to 1-phenyl-1-propyne. Evidence for this comes from the disappearance of physically adsorbed phenylallene (decrease in intensity of the infrared band at 1942 cm^{-1}) and the formation of 1-phenyl-1-propyne (development of weak infrared bands at 2250 and 2210 cm^{-1}). Conversely, phenylallene formed from the isomerization of 1-phenyl-1-propyne also transforms to 3-phenyl-1-propyne which then dissociates a hydrogen to yield an acetylide species $C_6H_5CH_2C{\equiv}C \ldots Zn$(surface). Evidence for this acetylide species is indicated by the observation, in both infrared and Raman spectra, of bands in the region 2080–2110 cm^{-1} following the adsorption of 1-phenyl-1-propyne. These bands are, as expected, very closely similar to those assigned to acetylide species resulting from adsorbed 3-phenyl-1-propyne.

In the case of homogeneous as well as heterogeneous catalysis, it is well known (*25*, *26*) that 1,2-alkadiene is formed as an intermediate product in the isomerization of 1-alkynes to 2-alkynes. In the present study, contrary to infrared spectra, Raman spectra obtained from adsorbed 3-phenyl-1-propyne and adsorbed 1-phenyl-1-propyne are not similar in that no phenylallene was observed in the Raman spectrum from the latter adsorbate. This probably suggests than an equilibrium state was not reached in the Raman experiments. It has been shown (*27*) that 2-butyne is thermodynamically more stable than 1,2-butadiene which in turn is more stable than 1-butyne. It is likely that the same order of stability also holds for the phenyl-containing compounds here. Estimation of the standard enthalpy of formation at 300°K of these compounds based on the group additivity method (*28*) indeed shows that their values are decreasing in this order ($C_6H_5CH_2C{\equiv}CH$, 71.7; $C_6H_5CH{=}C{=}CH_2$, 69.4; and $C_6H_5C{\equiv}CCH_3$, 68.7, all in kcal/mol). Conjugation of the phenyl ring with the side chain in the latter two compounds would be expected to give rise to their enhanced stability with respect to the former. It is probable that the

Raman samples, due to the experimental conditions used, could be less reactive than in the infrared experiments; this would lead to an equilibrium not being established with the majority of the compounds in the more stable forms. The different contributions of both infrared and Raman techniques to this study are of interest. It appears that the intermediate propargyllic species are observed only in the infrared spectrum which is in this case a more powerful technique to enable the elucidation of the mechanism of the isomerization reaction. Raman spectra, on the other hand, are not observable from the intermediate propargyllic species but readily indicate the presence of acetylide species resulting from the dissociation of 3-phenyl-1-propyne either as the starting compound or as the isomerization product.

ACKNOWLEDGMENTS

We thank the Science Research Council for support of this research program and Mr. Vallet for his help in the preparation of the compounds.

REFERENCES

1. Kokes, R. J., and Dent, A. L., *Adv. Catal.* **22**, 1 (1972).
2. Kokes, R. J., *Intra. Sci. Chem. Rept.* **6**, 75 (1972).
3. Kokes, R. J., *Accounts Chem. Res.* **6**, 226 (1973).
4. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92**, 6709 (1970).
5. Nguyen, T. T., and Sheppard, N., *J. Chem. Soc. Chem. Commun.* 868 (1978).
6. Saussey, J., Lavalley, J. C., and Sheppard N., *J. Chim. Phys.* **74**, 329 (1977).
7. Chang, C. C., and Kokes, R. J., *J. Catal.* **28**, 92 (1973).
8. Saussey, J., D.e. Sc. thesis, University of Caen, 1978.
9. Saussey, J., and Lavalley, J. C., *J. Chim. Phys.* **75**, 505 (1978).
10. Cooney, R. P., Curthoys, G., and Nguyen, T. T., *Adv. Catal.* **24**, 293 (1975).
11. Egerton, T. A., and Hardin, A. H., *Catal. Rev.* **11**, 71 (1975).
12. Nguyen, T. T., Cooney, R. P., and Curthoys, G., *J. Chem. Soc. Faraday Trans. I* **72**, 2577 (1976).
13. Egerton, T. A., Hardin, A. H., and Sheppard, N., *Canad. J. Chem.* **54**, 586 (1976).
14. Morimoto, T., Yanai, H., and Nagao, M., *J. Phys. Chem.* **80**, 471 (1976).
15. Mulvaney, J. E., Folk, T. L., and Newton, D. J., *J. Org. Chem.* **32**, 1674 (1967).
16. Chattopadhyay, S., *Ind. J. Phys.* **41**, 759 (1967).
17. Piaux, L., and Gaudemar, M., *Bull. Soc. Chim. France* 786 (1957).
18. (a) Lavalley, J. C., and Saussey, J., unpublished results; (b) Nguyen, T. T., *J. Catal.* **60**, in press (1979).
19. Damen, T. C., Porto, S. P. S., and Tell, B., *Phys. Rev.* **142**, 570 (1966).
20. Piaux, L., Gaudemar, M., and Henry, L., *Bull. Soc. Chim. France* 794 (1956).
21. Lord, R. C., and Ocampo, J., *J. Chem. Phys.* **19**, 260 (1951); Nyquist, R. A., Lo, Y. S., and Evans, J. C., *Spectrochim. Acta* **20**, 619 (1964).
22. Bourguel, M., and Daure, P., *Bull. Soc. Chim. France* **47**, 1349 (1930).
23. Murray, M. J., and Cleveland, F. F., *J. Amer. Chem. Soc.* **61**, 3546 (1940).
24. King, G. W., and So, S. P., *J. Mol. Spectrosc.* **36**, 468 (1970).
25. Jacobs, T. L., Akawie, R., and Cooper, R. G., *J. Amer. Chem. Soc.* **73**, 1273 (1951); Wojtkowiak, B., and Romanet, R., *Bull. Soc. Chim. France* 805 (1962).
26. Mortreux, A., and Blanchard, M., *Bull. Soc. Chim. France* 4035 (1970).
27. Rossini, F. D., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds." Carnegie Press, Pittsburgh, 1953; Saussey, J., Lamotte, J., Lavalley, J. C., and Sheppard, N., *J. Chim. Phys.* **72**, 818 (1975).
28. Benson, S. W., "Thermochemical Kinetics." John Wiley, New York, 1976.