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The Adsorption of Allylbenzene on Zinc Oxide: An Infrared Spectroscopic Study

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Infrared spectra from allylbenzene (or 3-phenyl-1-propene) ($C_6H_5CH_2CH{=}CH_2$) adsorbed on zinc oxide were recorded in the region 3800–1000 cm^{-1}. Dissociative chemisorption of allylbenzene occurs and yields an adsorbed phenylallyl species $[C_6H_5CHCHCH_2]^-$ which is characterized by $\nu_{asym}(CCC)$ = 1560 cm^{-1}. When allylbenzene is admitted to a zinc oxide disc containing preadsorbed hydrogen, adsorption of the phenylallyl species causes displacement of the latter from the surface. $\nu_{asym}(CCC)$ of the adsorbed phenylallyl species now appears at 1570 cm^{-1}. Prior to evacuation an additional physically adsorbed species is observed, tentatively identified as its isomer 1-phenyl-1-propene ($C_6H_5CH{=}CHCH_3$), possibly produced by catalytic hydrogen transfer.

INTRODUCTION

The function of zinc oxide as a base catalyst in heterogeneous reactions has been a subject of particular interest (*1*, *2*). The active sites on this oxide consist of site-pairs of Lewis acid–base type ($Zn^{2+}O^{2-}$), and it has been supposed (*2*, *3*) that the basic properties of the oxygen anions lead to dissociation of C–H bonds of hydrocarbons with pK values less than 36. For example, the chemisorption of propylene has been shown (*4*) to be dissociative and to involve fission of a methyl carbon–hydrogen bond to yield a hydrocarbon species and an OH species. Dent and Kokes (*4*) have described the adsorbed hydrocarbon species to be symmetrical, i.e., (CH_2CHCH_2), and π-allyl in nature. However, there remains more than one possible structure for such a species. Allyl groups can be σ-bonded, or π-bonded to neutral metal atoms, anionic $[C_3H_5]^-$ with respect to metal cations or cationic $[C_3H_5]^+$ with respect to nonmetal anions. Our reinvestigation of the propylene/ZnO system by means of Raman spectroscopy and Fourier transform infrared spectroscopy (*5*) has provided firm spectroscopic evidence for an anionic character of the adsorbed allyl species. Other spectroscopic studies using acetylenic compounds (*6*, *7*), including aromatic ones (*8*), and alkylbenzene (*3*) have also been reported. They all support the contention of Dent and Kokes that zinc oxide can function as a base catalyst toward appropriate carbon acids.

In catalytic terms, the allyl species obtained from propylene on heavy metal oxide catalysts is of industrial importance, and studies of propylene oxidation over zinc oxide still remain a subject of considerable interest (*9*, *10*). As part of our continued studies of unsaturated hydrocarbons on this oxide catalyst we report herein infrared spectra from adsorbed allylbenzene (i.e., 3-phenyl-1-propene) ($C_6H_5CH_2CH{=}CH_2$). By analogy with previous propene and butene results this aromatic olefinic compound would be expected to yield adsorbed phenylallyl species. Infrared spectra were also recorded of allylbenzene on zinc oxide containing preadsorbed hydrogen. Earlier studies have shown that preadsorption of propylene prevents subsequent dissociative adsorption of hydrogen (*4*), but molecular nitrogen or molecular hydrogen adsorption can occur at the same or nearby sites that concurrently adsorb hydrogen in the disso-

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ciative form (*11*). Therefore competitive interaction between allylbenzene and hydrogen for adsorption sites, as monitored by their infrared spectra, could provide some more information about these sites.

EXPERIMENTAL

Allylbenzene was obtained from the Aldrich Chemical Co., and was freshly redistilled at 157°C before use. Hydrogen of high-purity grade (99.6%) was obtained from BDH. ZnO powder was Kadox 15 from the New Jersey Zinc Company. The method of pretreatment of the ZnO disc has been described previously (*5*). Infrared spectra in adsorption experiments were recorded at 4-cm^{-1} resolution on a Digilab FTS 14 infrared interferometer. Spectra of the adsorbed species were obtained from the ratio of the spectrum of the oxide plus adsorbed species against that of the same oxide disc measured previously. Infrared spectra of allylbenzene in CCl_4 solution were obtained on a Perkin–Elmer 577 infrared spectrometer. To help in spectral assignments, Raman spectra of liquid allylbenzene were recorded on a Spex 1401 double monochromator coupled to a Coherent Radiation 52 mixed-gas argon–krypton ion laser. The exciting wavelength at λ = 488 nm was used.

RESULTS

1. Spectral Assignments of Allylbenzene

There has been no reported assignment of the vibrational spectrum of pure allylbenzene in the literature; only its Raman spectrum was summarized in an early study (*12*). The infrared and Raman spectra of allylbenzene obtained in the present study are listed in Table 1. For comparison with spectra from adsorbed species we are mainly interested in the region above 900 cm^{-1} as the low-frequency ZnO cutoff begins at this position in the infrared spectrum.

TABLE 1

Infrared and Raman Spectra (cm^{-1}) of Allylbenzene ($C_6H_5CH_2CH{=}CH_2$)

Infrared (in CCl_4 solution)	Raman (pure liquid)
915 (vst)	917 (vw)
990 (vst)	991 (sh)
	1005 (vst)
1032 (st)	1032 (m)
1074 (m)	
1110 (w)	
1158 (vw)	1158 (w)
1180 (m)	1179 (w)
1192 (sh)	1195 (m)
1285 (m)	
1297 (m)	1297 (m)
1330 (w)	
1340 (sh)	
1358 (vw)	
1382 (w)	
1413 (m)	1414 (w)
1432 (vst)	1436 (w)
1440 (sh)	
1453 (vst)	
1470 (sh)	
1494 (vst)	
1585 (sh)	1586 (w)
1600 (vst)	1605 (w)
1638 (vst)	1641 (st)
1802 (m)	
1830 (m)	
1940 (m)	
1957 (w)	
2835 (m)	2840 (w)
2902 (vst)	2906 (m)
	2918 (sh)
2980 (vst)	2984 (m)
3006 (w)	3008 (m)
3030 (vst)	3058 (st)
3065 (vst)	3068 (sh)
3087 (vst)	3080 (sh)
3100 (sh)	3110 (vw)

Note. Abbreviations used: w = weak, vw = very weak, m = medium, st = strong, vst = very strong, sh = shoulder.

We are only concerned here with the assignment of the more prominent features in the infrared and Raman spectra (*12–15*) for comparison with spectra from the adsorbed species. Aromatic ring skeletal vibrations give rise to bands near 1600, 1585, 1494, 1453, 1032, and 1005 cm^{-1}. A stretching mode, in part localised in the C–C bond attached to the aromatic ring, occurs at 1195 cm^{-1} (*14*). Characteristic strong bands of the vinyl group occur near 1640, ν

(C=C); 1413, δ (=CH_2); 1297, δ (=CH); 990 and 915 cm^{-1}, γ (CH)/γ (CH_2) out-of-plane modes. The δ (CH_2) scissor mode occurs at 1432 cm^{-1}.

In the ν (CH) region, aromatic bands occur near 3060 and 3030 cm^{-1}, and vinyl modes probably at 3087, ν_{asym} (=CH_2); 3008, ν (=CH); and 2980 cm^{-1}, ν_{sym} (=CH_2). The ν_{sym} (CH_2) mode occurs near 2905 cm^{-1}, and the ν_{asym} (CH_2) mode is probably overlapped with the vinyl band near 2980 cm^{-1}. The remaining prominent feature at 2835 cm^{-1} can be attributed to Fermi resonance of δ (CH_2) with ν_{sym} (CH_2).

2. *Allylbenzene Adsorption on ZnO*

A number of remarkable spectral changes occurred following adsorption of allylbenzene on zinc oxide. Since the region below 1000 cm^{-1}, observed by spectral ratioing, is poorly infrared-transmitting we will limit description of spectra to above 1000 cm^{-1}. The infrared results from adsorbed species are summarized in Table 2.

(*a*) *The region 1700–1000* cm^{-1}. This region of the spectrum obtained after evacuation of the gas phase is shown in Fig. 1. Prior to evacuation a weak additional band occurred at 1640 cm^{-1} which could be attributed to the physically adsorbed allylbenzene, as its frequency is very close to that (1638 cm^{-1}) observed in the liquid state. The presence of an allyl-type species, which we shall presume to be carbanionic as from propylene on ZnO (*5*), is clearly shown by an intense band at 1560 cm^{-1} in agreement with previous propylene results (*4*). The formula of this species is presumed to be $[C_6H_5CH{\cdots}CH{\cdots}CH_2]^-$, and the band in question is assigned to the ν_{asym} (C⩦C⩦C) mode. Another intense band at 1290 cm^{-1} probably originates in a CH in-plane deformation mode of the anionic group; a band at this position in the spectrum of allylbenzene is much weaker. The presence of a single δ (CH_2) absorption near 1420 cm^{-1} (cf. 1413 *and* 1432 *cm*$^{-1}$ *for the parent hydrocarbon*) is also

TABLE 2

Infrared Spectra (cm^{-1})[a] of Adsorbed Species from Allylbenzene on Zinc Oxide Alone and on Zinc Oxide Containing Preadsorbed Hydrogen

Adsorbed on ZnO alone (after evacuation)	Adsorbed on ZnO containing preadsorbed hydrogen (before evacuation)[b]
1025 (m)	1020 (m)
1075 (mw)	1074 (mw)
1110 (vw)	1107 (vw)
1150 (m)	1143 (m)
1170 (sh,w)	1172 (w)
1210 (w)	1210 (w)
1260 (sh,m)	1250 (w)
1290 (st)	1287 (m)
	1300 (sh)
1325 (w)	1325 (w)[c]
1340 (w)	1340 (w)
1385 (w)	1375 (w)
1420 (sh,w)	1420 (w)
1450 (m)	1448 (m)
1500 (vst)	1490 (st)
	1515 (sh,m)[c]
	1560 (sh,m)
1560 (vst)	1570 (st)
1580 (st)	1584 (vst)
1600 (sh)	
	1640 (w)[d]
1670 (vw)	1660 (w)[d]
2740 (vw)	
2862 (w)	2857 (w)
	2900 (m)
2925 (st)	2920 (m)
2942 (st)	2940 (w)
2968 (st)	2958 (st)
2995 (vw)	~2995 (vw)
3030 (vst)	3025 (st)
	3050 (m)
3065 (st)	3062 (st)
3082 (sh,w)	3082 (w,sh)
3105 (sh,vw)	
3520 (m)	3515 (m)
3594 (m)	3590 (m)

[a] Spectra were ratioed against ZnO background; w = weak, vw = very weak, m = medium, st = strong, vst = very strong, sh = shoulder.

[b] Bands at 1710 and 3495 cm^{-1} due to preadsorbed hydrogen disappeared on adsorption of allylbenzene.

[c] The intensities and positions of these bands may be somewhat in error because of inaccurate cancellation of background absorptions.

[d] Only these features disappeared after evacuation, other bands remained virtually unaffected.

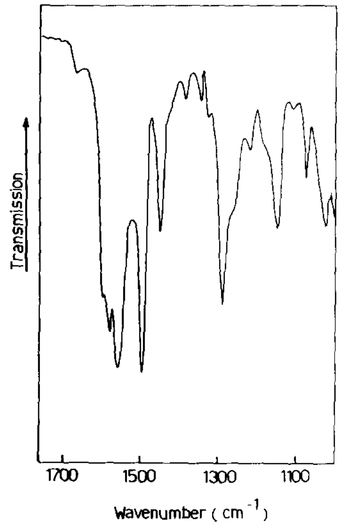


FIG. 1. Infrared spectrum of adsorbed species from allylbenzene on zinc oxide in the region 1700–1000 cm^{-1} obtained after evacuation.

consistent with removal of the hydrogen atom from the CH_2 group of allylbenzene. A prominent band at 1150 cm^{-1} is probably associated with a side-chain skeletal mode partly localised in the C–C bond next to the aromatic ring. Bands at 1600 (shoulder), 1580, 1500, 1450, and 1025 cm^{-1} probably correspond to the analogous aromatic ring skeletal modes of the parent hydrocarbon.

(*b*) *The region 3200–2800 cm^{-1}.* The most intense absorption at 3030 cm^{-1} and its companion at 3065 cm^{-1} (Fig. 2a) can be assigned to ν (CH) modes of the aromatic ring. Absorptions at 2968, 2942, and 2925 cm^{-1} probably represent three of the four ν (CH) fundamentals of the side-chain of the anionic species. Weaker bands at 2995 and 2862 cm^{-1} provide alternative possibilities for the fourth ν (CH) mode. We favour the higher wavenumber as the resulting mean ν (CH) value then closely corresponds to that obtained from the ν (CH) modes of the allyl carbanion derived from propylene (5). A very weak shoulder at 3082 cm^{-1} may represent the ν_{asym} ($=CH_2$) mode of a small proportion of residual physically adsorbed or π-bonded species.

(*c*) *The region 3700–3400 cm^{-1}.* The zinc oxide studied by itself has four distinct OH bands at 3450 (broad, medium), 3595 (sharp, very weak), 3620 (sharp, medium), 3642 (sharp, very weak), and 3670 (broad, medium) (see Fig. 3a). Upon allylbenzene adsorption two intense and broadened features formed near 3520 and 3595 cm^{-1} (see Fig. 3c). Spectral ratioing techniques clearly show that the former results from substantial displacement of the background OH band at 3670 cm^{-1} due to hydrogen bonding interaction, whereas the latter arises from the newly formed OH species in the dissociative chemisorption. Again the present results are consistent with previous observations from phenylpropynes (*8*), ethynylbenzene (*16*), and toluene (*17*) adsorbed on zinc oxide. In particular, the 3595-cm^{-1} band here is in good agreement with propene adsorption results (*4*).

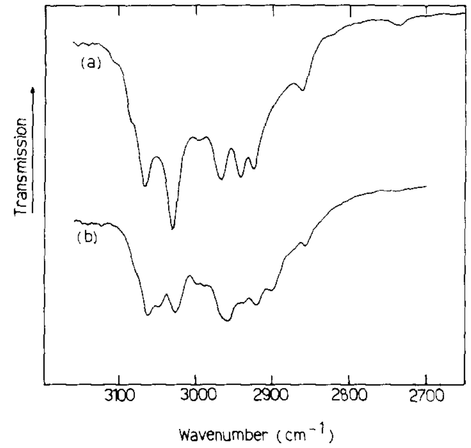


FIG. 2. Infrared spectra of adsorbed species from allylbenzene in the region 3200–2700 cm^{-1}: (a) on ZnO without hydrogen preadsorption and after evacuation; (b) on ZnO containing pre-adsorbed hydrogen and before evacuation.

3. *Allylbenzene Adsorption on ZnO Containing Preadsorbed Hydrogen*

In a separate experiment, hydrogen was first admitted to a pretreated zinc oxide disc. Dissociative adsorption occurred as indicated by two intense bands at 1710 and 3497 cm^{-1} (the latter is shown in Fig. 3b), which have previously been assigned (*18*)

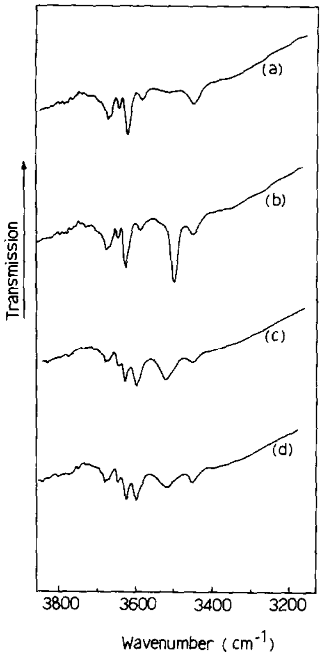


FIG. 3. Infrared spectra in the OH stretching region (3800–3300 cm^{-1}); (a) ZnO background; (b) hydrogen preadsorption, before evacuation; (c) allylbenzene adsorption on ZnO containing preadsorbed hydrogen, before evacuation (this spectrum is very similar to that in the case without hydrogen preadsorption); (d) spectrum (c) after evacuation of gaseous phases for 40 min at room temperature.

to ZnH and OH stretching bands. Allylbenzene was then admitted. The resultant spectrum, recorded before evacuation, is summarized in Table 2. The bands due to dissociatively adsorbed hydrogen disappeared completely. In the region 1600–1000 cm^{-1} (Fig. 4) bands are found which are, in general, similar to those observed in the absence of preadsorbed hydrogen, but they differ in their relative intensities and precise positions. The formation of an adsorbed allylic carbanionic species once again is indicated by bands at 1570 and 1287 cm^{-1}. Both of these are weaker (relative to skeletal bands from the aromatic rings) than previously, but they are still prominent, showing that this species is an important one. The shift of the ν (CCC) mode from 1560 to 1570 cm^{-1} may be caused either by a slightly different environment on the surface due to preadsorbed hydrogen, or possibly to a different conformation of the allylic species (see below). A sharp transmission maximum near 1535 cm^{-1} is caused by a shift of a carboxylate absorption present in the background spectrum of the zinc oxide that was used for ratioing. This shift could be seen in the nonratioed spectra which exhibited carboxylate bands of 20 to 25% absorption. Little shift occurs in the companion carboxylate band near 1330 cm^{-1} but possible uncertainties in both these regions of the ratioed spectra are nevertheless indicated in Table 2. Although

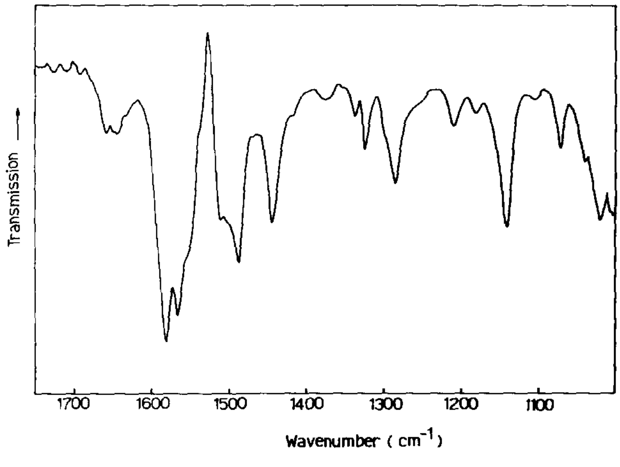


FIG. 4. Infrared spectrum of adsorbed species from allylbenzene on zinc oxide with preadsorbed hydrogen in the region 1700–1000 cm^{-1} obtained before evacuation.

similar carboxylate absorptions occurred in the background spectra from the non-hydrogen-covered ZnO experiments, these were substantially weaker relative to the spectra of the adsorbed species and no real uncertainty from this cause is thought to occur in the ratioed spectrum of Fig. 1. A band shift in the background of course causes adjacent positive and negative lobes in the ratioed spectra.

The observation of the usual new ν (OH) band at 3595 cm^{-1} on adsorption of the allylbenzene, plus the broad band at 3520 cm^{-1} caused by hydrogen bonding (see Fig. 3c and compare with Fig. 3b), strongly confirms the presence of allylic species (*4*, *5*).

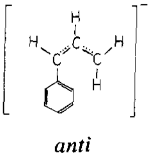
An additional weak overlapping pair of bands with maxima at 1660 and 1640 cm^{-1} is present in this spectrum as shown in Fig. 4; these both pump away on evacuation for 40 min at room temperature. The 1640-cm^{-1} band most probably denotes the presence of physically adsorbed allylbenzene (3-phenyl-1-propene). The origin of the 1660-cm^{-1} band is less clear. One possibility (see below) is that it denotes the presence of the physically adsorbed 1-phenyl-1-propene ($C_6H_5CH{=}CHCH_3$) isomer of allylbenzene. The *trans* geometrical isomer of these compounds shows a band of medium strength near 1660 cm^{-1} in its infrared spectrum (*15*). Such an isomer is expected to be produced by hydrogen transfer on the ZnO catalyst. The presence of more abundant physically adsorbed species, compared with adsorption on the catalyst without preadsorbed hydrogen, probably accounts for the greater relative intensities of the aromatic skeletal absorptions compared with the substituted allyl anion band at 1570 cm^{-1}.

Although the overall spectral profile obtained in the 3000-cm^{-1} region before pumping (Fig. 2b) is not dissimilar to that obtained in the absence of preadsorbed hydrogen, the bands are generally broader. This is also consistent with the presence of appreciable amounts of several adsorbed species. The physically adsorbed species probably give rise to weak extra absorptions at 3050 and 2900 cm^{-1}, and additional intensity near 3062, 2958, and 3082 cm^{-1}. The presence of the expected hydrogenated product *n*-propylbenzene is not evident in the spectrum (e.g., a lack of strong absorptions near 2920 cm^{-1}, ν_{sym} (CH_2): or 1380 cm^{-1}, δ_{sym} (CH_3)). However, such a constituent would probably be more weakly adsorbed and its infrared absorptions would be much weaker if it existed in the large-volume vapour phase. After pumping for 40 min at room temperature, the spectrum in the region 3200–2700 cm^{-1} in general became weaker but showed no remarkable changes in absorption positions compared to that recorded before evacuation.

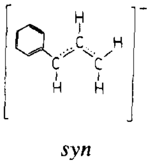
DISCUSSION

1. *Allylbenzene Adsorption on ZnO*

By analogy with the case of adsorbed propylene, the presence of the prominent bands at 1560, ν (CCC), and at 3595 cm^{-1}, ν (OH), almost certainly denotes the formation of a dominant phenylallyl anionic species of formula $[C_6H_5CH\cdots CH\cdots CH_2]^-$ from adsorbed allylbenzene. The difference between the wavenumbers of the ν (CCC) bands and those of the ν (C=C) absorptions of the parent hydrocarbons (-78 cm^{-1} for allylbenzene compared with -107 cm^{-1} for propylene) is probably caused by partial delocalisation of the negative charge in the aromatic compound away from the side chain, also leading possibly to weaker adsorption interactions with Zn^{2+} ions. The anionic species depicted above could have two conformations, *syn* and *anti*, as shown below.



anti



syn

A study by Chang *et al.* (*19*) of analogous isomers derived from *cis*- and *trans*-2-butene suggests that the *anti* and *syn* conformations have ν (CCC) absorptions at distinguishable wavenumbers, and they favour the attribution of the prevailing ν (CCC) absorption to the more stable *anti* form. However, it is difficult to tell whether there are two ν (CCC) bands present here because of overlapping aromatic ring absorptions. By analogy with published 1-butene results, the band at 1560 cm^{-1} could be attributable to the *anti* conformation. The observation of a weak band near 1670 cm^{-1} may denote the presence of a smaller proportion of another species having a different structure. In the case of propylene adsorption a persistent weak band near 1610 cm^{-1} was also noted (*20*).

2. *Allylbenzene Adsorption on ZnO Containing Preadsorbed Hydrogen*

Adsorption of allylbenzene on ZnO containing preadsorbed hydrogen causes major displacement of the latter from (Zn^{2+} O^{2-}) pair sites by the newly adsorbed species. Previous results (*4*) showed that preadsorbed propylene blocked nearly all the sites active in Type I hydrogen adsorption. These active sites consist of only a limited number of isolated zinc oxide ion pairs which are capable of heterolytic fission (*2*,, *21*, *22*). We presume that the slightly higher wavenumber of ν_{asym} (CCC) (1570 cm^{-1}), compared to that observed in the absence of preadsorbed hydrogen (1560 cm^{-1}), reflects the slight perturbation of the adsorbed phenylallyl by some residual hydrogen species probably of Type II at nearby sites. Adsorbed hydrogen of Type II is nonobservable in the infrared and is strongly held at room temperature (*22*). The observation of a weak satellite near 1560 cm^{-1} probably suggests the presence of a much smaller proportion of adsorbed species at unperturbed Type I sites. The alternative attribution of the prominent higher wavenumber band at 1570 cm^{-1} to another conformation of the anion (*19*) is possible but perhaps less likely.

Isomerization of allylbenzene ($C_6H_5CH_2CH{=}CH_2$) to 1-phenyl-1-propene ($C_6H_5CH{=}CHCH_3$) is expected over zinc oxide in the presence of hydrogen and (see earlier discussion) could be responsible for the observation of the feature near 1660 cm^{-1} assignable to the latter physically adsorbed isomer. In contrast to this, in the absence of preadsorbed hydrogen, the spectrum before evacuation of the gas phase contained only a band at 1640 cm^{-1} (i.e., almost the same position as the liquid value) due to physically adsorbed allylbenzene. An alternative explanation for the 1660 cm^{-1} band is that it represents residual ν ZnH from Type I adsorbed hydrogen that has been shifted due to interaction with adsorbed hydrocarbon species (*23*). We note that over thorium dioxide, ThO_2, the activity of the catalyst in the isomerization of 1-butene is enhanced by treatment with hydrogen but reduced by treatment with oxygen (*24*). Mention should also be made of the isomerization of allylbenzene to 1-phenyl-1-propene catalyzed (*25*) by the metal hydrocarbonyl $HCo(CO)_4$.

ACKNOWLEDGMENT

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