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An Infrared Study of Isomerization of Cyclo-Olefins over Zinc Oxide

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Infrared studies of olefin hydrogenation and isomerization over zinc oxide have led successfully to greater understanding of the nature of adsorption and reaction mechanisms on metal oxide catalysts. Previous studies have shown that, for the simplest olefin, ethylene, the mode of adsorption is via a π-bonded species; hydrogenation occurs through a half-hydrogenated ethyl radical intermediate. In addition for propylene, two adsorbed species occur—a π-bonded complex and a π-allylic species. Hydrogenation occurs via the π-bonded complex, whereas isomerization of (deutero) propylenes proceeds through the π-allylic complex. The complexity of the system increases markedly as the complexity of the olefins increases. This paper describes the results of an extension of these studies to cyclo-olefin systems which include cyclobutene, methylenecyclobutane, and cyclopentene. For cyclopentene, infrared studies indicate that the dominant adsorbed species appear to be π-bonded species. For cyclobutene, studies suggest that apparently ring opening accompanies adsorption. Infrared evidence indicates a strong similarity between the adsorbed species and that from 1,3-butadiene. For methylenecyclobutane, exo–endo isomerization leads to 1-methylcyclobutene with a common π-allylic intermediate. Volumetric and ir adsorption studies substantiate the results. For example, strong evidence exists for the presence of two π-bonded species which are precursors of the π-allylic intermediate from their respective directions. In addition, catalytic batch recycle reactor studies indicate the system has an apparent activation energy of 14.0 ± 1.0 kcal/mole.

INTRODUCTION

Hydrogenation and isomerization of olefins are classic examples of heterogeneous catalytic reactions. Both metals and metal oxides are catalysts for these reactions. The prevailing evidence to date suggests that there is a fundamental difference in the reaction mechanism for metals as compared to metal oxides (*1*, *2*). Isomerization of olefins over metals during catalytic hydrogenation proceeds via the pathway (*2*):

$$\mathrm{R{-}CH_2{-}CH{=}CH{-}R' + H{-}{*} \rightleftarrows R{-}CH_2{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2{-}R'}, \tag{1}$$

$$\mathrm{R{-}CH_2{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2{-}R' + 2{*} \rightleftarrows R{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2{-}R' + H{-}{*}}, \tag{2}$$

$$\mathrm{R{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}}\underset{*}{\mathrm{CH}}\mathrm{{-}CH_2{-}R' \rightleftarrows R{-}CH{=}CH{-}CH_2{-}R' + 2{*}}. \tag{3}$$

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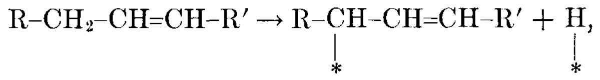
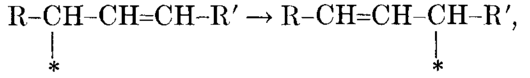
It is seen that hydrogen adatoms must act as cocatalysts for the olefin isomerization reaction.

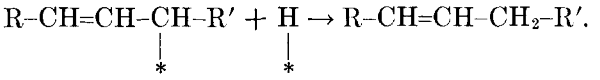
Over oxide catalysts such as chromia (*3*) and zinc oxide (*4*, *5*) studies reveal several features which support an alternate isomerization pathway. The most important of these is isomerization occurring in the *absence* of hydrogen over chromia. Burwell *et al.* (*3*) suggested that allylic species may furnish an isomerization pathway which does not require the alkyl reversal (step 2) needed for metals, viz.,



$$\mathrm{R{-}CH_2{-}CH{=}CH{-}R'} \rightarrow \mathrm{R{-}}\underset{*}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH{=}CH{-}R'} + \underset{*}{\underset{|}{\mathrm{H}}}, \qquad (4)$$



$$\mathrm{R{-}}\underset{*}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH{=}CH{-}R'} \rightarrow \mathrm{R{-}CH{=}CH{-}}\underset{*}{\underset{|}{\mathrm{CH}}}\mathrm{{-}R'}, \qquad (5)$$



$$\mathrm{R{-}CH{=}CH{-}}\underset{*}{\underset{|}{\mathrm{CH}}}\mathrm{{-}R'} + \underset{*}{\underset{|}{\mathrm{H}}} \rightarrow \mathrm{R{-}CH{=}CH{-}CH_2{-}R'}. \qquad (6)$$

Recent studies by Dent and Kokes (*4–6*) have provided convincing infrared evidence for the support of such allylic species over zinc oxide catalysts. These studies have shown that, whereas ethylene adsorption occurs principally through the interaction of the π-electrons with the surface site to form a π-bonded, adsorbed species, propylene adsorption involves an additional more strongly bonded species which has been identified via deutero isotopes as a π-allylic species. More recently, Gay and Whitney (*7*) through their NMR studies of ethylene and propylene adsorbed on zinc oxide confirmed the assignments of Dent and Kokes (*5*, *6*). In the case of butene isomerization (*8*, *9*) the situation is further complicated by an additional stereochemical factor. For example, the adsorption of butene-1 can lead to at least five possible surface species, namely, π-*cis*-butene-2, π-*trans*-butene-2, π-butene-1, syn-π-allyl, and anti-π-allyl. (The adsorbed species of propylene and the butenes are shown in Fig. 1.) Of the possible π-allyls, the anti-π-allyl is formed preferentially when butene-1 chemisorbs on zinc oxide (*9*). *Cis*-butene-2 and *trans*-butene-2 from the anti-π-allyl and syn-π-allyl, respectively.

The combination of infrared techniques with kinetic studies (*4–6*, *9*, *10*) provided information about the reactivity of the various adsorbed species during catalytic hydrogenation. For ethylene, these studies have shown that the π-bonded ethylene reacts on the surface with type I chemisorbed hydrogen (*4*, *5*). For propylene, Naito and co-workers (*10*) have confirmed that the π-allylic species is the active intermediate in the isomerization of "labeled" propylenes and intermolecular hydrogen exchange, but that the π-bonded species is the active intermediate in hydrogenation of the olefin. The π-allylic species has been shown to be the active intermediate in the formation of acrolein during the oxidation of propylene on zinc oxide (*11–13*). Similarly, the role of the five surface species during butene isomerization has been investigated (*9*).

As the size of the olefin increases, the complexity of the adsorbed species increases correspondingly. The complexity may arise from the number of surface species participating in the isomerization reactions or from the molecular complexity of the adsorbed species—stereochemistry. The study of cyclic olefins affords the opportunity to assess further

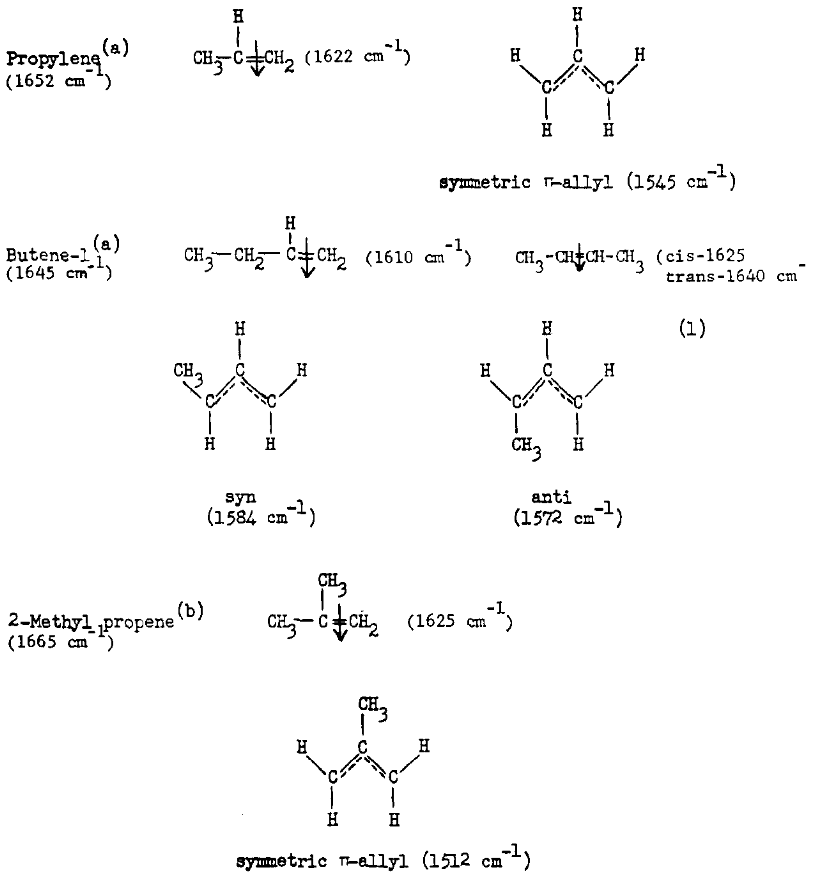


FIG. 1. Structure of adsorbed intermediates on zinc oxide. (a) Assigned by Dent and Kokes (*4*); (b) assigned in this work; (1) preferred species on the surface.

the role of stereochemistry with respect to which species plays the dominant role on the surfaces. This paper reports in part the isomerization studies conducted on a number of cyclic olefins and related compounds over zinc oxide. Included in these studies are cyclopentene, cyclobutene, methylenecyclobutane, 1,3-butadiene, 1,4-pentadiene, cyclopropane, and 2-methylpropene.

METHODS

Materials. The zinc oxide used in this work was Kadox 25 obtained from the New Jersey Zinc Co. Research-grade propylene, 1,3-butadiene, 2-methylpropylene, and cyclopropane were supplied by Matheson Scientific Co. Methylene-cyclobutane (99%) and cyclobutene (97%) were purchased from the Chemical Sample Co. Aldrich Chemical Co. supplied 1,4-pentadiene (99%) and cyclopentene (99%). All of the above gases or liquids were purified by bulb to bulb distillation of the vapor phase only, with liquid nitrogen freezing and evacuation of the noncondensible traces of impurity gases. Infrared spectra of the gases were determined and compared with those from American Petroleum Institute (API) infrared tables (*14*). In addition, gas chromatographic analyses of the samples were determined using a 4.6 mm × 1.83 m column of silver nitrate in ethylene glycol supported on firebrick (*15*). A Perkin-Elmer vapor fractomer, Model 154C instrument fitted with a TC detector was coupled with a Varian Scientific Instruments' CDS-101 data processor to achieve gas separation and peak area integration.

Tank oxygen was purified in a manner similar to that used for the hydrocarbons. Tank hydrogen, deuterium, helium, and nitrogen supplied by West Penn AIRCO, Inc., were purified by passage through an activated charcoal trap maintained at 78°K and stored in 5-liter bulbs on the vacuum system.

Volumetric adsorption studies. Adsorption measurements using a standard multipurpose vacuum system were accomplished with 20-g samples of the zinc oxide which had been pressed into disks and broken into smaller pieces. Activation of the sample was achieved by (i) degassing while increasing the temperature to 723°K; (ii) calcining in 0.208 atm of oxygen at this temperature for 1 hr; (iii) degassing for another 1 hr; (iv) repeating steps 2 and 3 for 0.5 hr; (v) readmitting oxygen and cooling to room temperature before degassing the oxygen for at least 0.5 hr. Following activation, 0.0130 atm of the appropriate gas under study was admitted to the sample cell for 30 min through the BET (*16*) portion of the vacuum system. The total amount of gas adsorbed could be separated into: (a) weakly bond material which was removable by liquid nitrogen trapping or evacuation at room temperature for 0.5 hr and (b) "irreversibly" adsorbed material which could only be removed by degassing at higher temperatures, typically 398°K for 0.5 hr and 673°K for 0.5 hr. At each temperature, the amount of material desorbed was determined and the total amount of material recovered from the surface could also be assessed. After the 673°K degassing period the total surface area of the sample was measured by the BET method using nitrogen at 78°K.

Infrared adsorption studies. ZnO samples weighing between 0.6 and 0.7 g were pressed into disks under a pressure of approximately 700 atm in a stainless steel sample holder. The disk (125 mg/cm^2 of geometric area) was centered in the "elevator" cell by the use of a fine nichrome wire attached to a windlass. The sample could be raised into the furnace area or lowered between the infrared windows as desired. Tubulations with stopcocks permitted gases to be introduced into the ir cell when the cell was attached to an auxiliary vacuum system via ball joints. *In situ* activation was achieved using the same procedure employed for the volumetric adsorption measurement. This activation procedure yielded samples with excellent transmission properties, e.g., 55% transmission at 1250 cm^{-1} was typical. All infrared spectra were recorded with a Beckmann Model 4250 grating double-beam spectrometer with spectral slits of 10 cm at 4000 cm^{-1} and 5 cm at 1400 cm^{-1}. All spectra were recorded with the sample at ambient temperatures, nominally 298°K, but probably somewhat higher due to heating by the ir beam (*17*).

In each case prior to gas admission to the cell, a background scan of the activated zinc oxide was recorded and is shown in the spectra reported for adsorbed olefins as a dotted line.

Infrared adsorption studies were obtained with an olefin pressure of 0.0130 atm in both the sample cell and the reference cell. In some cases the olefin was admitted as 0.0130 atm of a 5% olefin in helium mixture.

Kinetic studies. Methylenecyclobutane isomerization studies were conducted in a batch recycle reactor with forced circulation of gas mixtures (12.5 liters min^{-1}) achieved by a metal bellows pump (Met-Bel) purchased from the Cole Parmer Co. Figure 2 is a schematic diagram of the 0.560 *l* reactor loop. Isomerization studies were determined using 5- and 20-g samples prepared and activated in the manner described for the adsorption studies. The

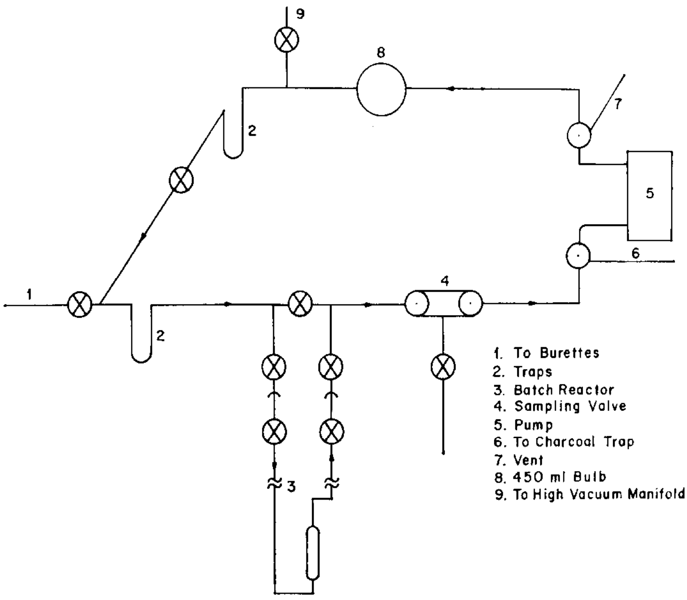


FIG. 2. Batch recycle reactor loop.

U-tube catalyst cell was immersed in a constant-temperature bath regulated by a Nanmac temperature controller to within ±0.3°C. Samples of the reaction mixture were withdrawn for gas chromatographic analysis through position 4 in Fig. 3. Each sample caused a 1.5% decrease in the total pressure. These samples were collected in 500-ml bulbs and transferred to the gas sampling loop of a six-port gas-sampling valve on the gc by pumping with a liquid N_2 trap on the loop. The gc column was operated at 303°K (*15*).

Mixtures of methylenecyclobutane and

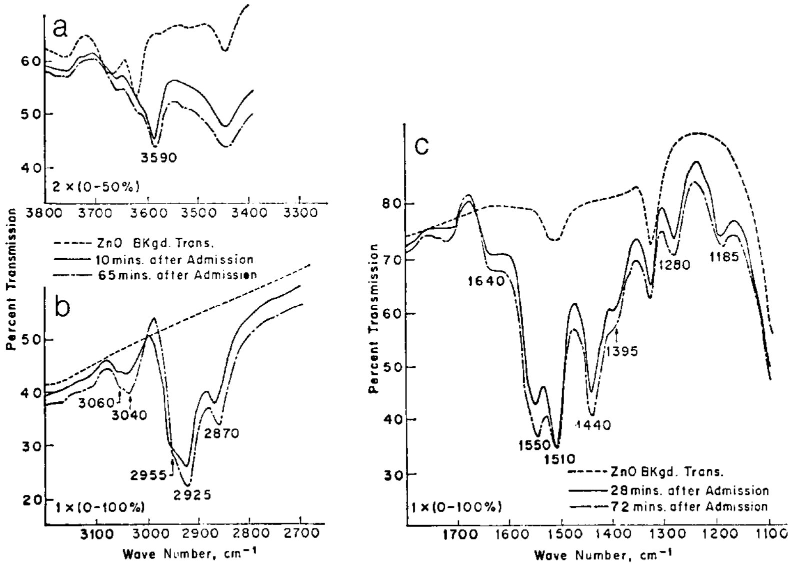


FIG. 3. Methylenecyclobutane on Kadox 25 zinc oxide. Sample and reference-cell pressure = 0.0130 atm; (a) O–H stretching region; (b) C–H stretching region; (c) C–C stretching and C–H bending regions.

helium were circulated over the catalyst at the desired temperature. Progress of the reactions was determined by gc analysis of the samples collected as described above. All gc analyses were considered to be accurate to ±3% of the recorded value.

RESULTS AND DISCUSSION

Volumetric Adsorption Studies

Tables 1 and 2 summarize the results of the volumetric adsorptions at 298°K and 328°K, respectively. The second column in each table is self-explanatory and gives the total number of molecules of olefin adsorbed per 100 Å^2 based on the surface area as reported in column 5. This value included the contributions due to physically, weakly, and strongly adsorbed species. This total represents about 20% of the total surface coverage and is approximately equal to that found in an earlier work for ethylene adsorption on zinc oxide (*4*). Column 3 represents the amount of strongly chemisorbed species on the surface and is indicative of the amount of π-allylic species present. The difference between columns 2 and 3 represents the amount of physically and weakly chemically adsorbed species. Since the relative pressure (P/P_0) for all of the olefins is close to 0.01, we would anticipate that this represents essentially the weakly chemisorbed material, i.e., physical adsorption is minimal under these conditions. Column 4 represents the material balance on column 3. If all of the material is desorbed in a condensible form, these two columns would be identical.

Several features arise from an analysis of these data. The results for cyclopropane indicate that about half of the adsorbed material is weakly bonded. The remaining material is removed by degassing at 398°C for about 1 hr. In general, the distribution among the various adsorbed species is similar for all other compounds studied. It is seen that approximately 25–30% of

TABLE 1

Adsorption of Olefins at 298°K[a]

Reactant	Total amount adsorbed (mol/100 Å^2)	Amount irreversibly adsorbed[b] (mol/100 Å^2)	Amount desorbed[c] (mol/100 Å^2)	Total surface area[d] (m^2/g)
Propylene	1.94	1.48	1.47	7.0
2-Methylpropene	2.05	1.59	1.52	7.0
	2.04	1.58	1.51	6.9
Methylenecyclobutane	2.28	1.80	1.27	4.5
	2.39[e]	1.92	1.35	4.0
Cyclobutene	2.05	1.58	1.21	6.1
	2.00	1.52	1.34	6.8
Cyclopropane[f]	1.60	0.81	0.62	8.2
1,3-Butadiene	1.84	1.26	1.06	5.3
1,4-Pentadiene	2.16	1.71	0.67	5.3

[a] Adsorbed pressure of gases was 0.0130 atm over 20 g of zinc oxide catalyst.

[b] Amounts left after degassing for 0.5 hr at room temperature.

[c] Amounts desorbed by degassing at 398°K for 0.5 hr and at 673°K for 0.5 hr, including possible products of reactions (condensibles) in some cases.

[d] Total surface area measured by BET method using nitrogen at 78°K.

[e] Adsorption at 298°K for 4 hr.

[f] Adsorbed pressure of cyclopropane was 0.041 atm on 5.0 g of ZnO catalyst. Desorption at 398°K for 1 hr.

TABLE 2

Adsorption of Olefins at 328°K[a]

Reactant	Total amount adsorbed (mol/100 Å^2)	Amount irreversibly adsorbed[b] (mol/100 Å^2)	Amount desorbed[c] (mol/100 Å^2)	Total surface area[d] (m^2/g)
2-Methylpropene	1.71	1.33	1.26	6.9
	1.76	1.31	1.25	7.2
Methylenecyclobutane	1.68	1.30	1.25	7.0
	1.67	1.25	1.20	6.3
Cyclobutene	1.70	1.18	0.95	6.8
	1.68	1.17	0.89	5.9
Cyclopentene	1.76	1.26	0.86	6.8
	1.65	1.21	0.79	6.2
1,4-Pentadiene	1.62	1.38	1.07	5.4

[a] Adsorbed pressure of gases was 0.0130 atm over 20 g of ZnO catalysts.

[b] Amounts left after degassing for 0.5 hr at 328°K.

[c] Amounts left by degassing at 398°K for 0.5 hr and at 673°K for 0.5 hr, including products of reactions (condensibles) in certain cases.

[d] Total surface area measured by BET method using nitrgen at 78°K.

the total adsorption occurs as "π-bonded" species. All of the propylene was removed by degassing between room temperature and 398°K (*6*) and most of the chemisorbed 2-methylpropene was removed under similar conditions. However, with the dienes and cyclo-olefins a considerable discrepancy results between room temperature and 673°K. There is generally a 25% loss of material which is probably due to side reactions such as dimerization, dehydrogenation and/or polymerization. In the methylenecyclobutane studies, infrared and mass spectroscopic and gas chromatographic analyses of the materials desorbed at room temperature, 398°K, and 673°K were made to identify possible products. These results confirmed that 1-methylcyclobutene was desorbed between room temperature and 398°K. Degassing above 398°K gave a product which appeared to be 1,4-pentadiene, 1,3-pentadiene, or 2-methyl-1,3-butadiene, the nature of which is discussed under infrared studies. However, the major product of the isomerization of methylenecyclobutane at temperatures ranging from room temperature to 398°K is 1-methylcyclobutene. Thus, the column in Tables 1 and 2 for the dienes and cyclo-olefins may show both kinds of desorbed materials, starting hydrocarbons, and products. In addition, it is noted that increasing the adsorption temperature to 328°K had no appreciable effect on the distribution of adsorbed species. Furthermore, changing surface areas of the zinc oxide had negligible effects on the results for the compounds studied.

Infrared Adsorption and Kinetic Studies

The primary focus of this discussion will be on the studies involving methylenecyclobutane. Only a brief summary of the results for other compounds will be attempted. First, 2-methylpropene infrared studies resulted in spectra which were predictable from the earlier work on propylene and butene-1 (*4*). The $\nu_{C=C}$ frequencies are summarized in Fig. 1 and indicate an appreciable decrease in the π-allylic frequency due to the methyl group on the central carbon atom. Studies with cyclopropane were included because of its reported isomerization via ring opening (*18*). As Table 1 indicates, approximately half of the adsorbed material is strongly adsorbed. However, exhaustive infrared studies showed only evidence for physically adsorbed species. In the absence of the gas phase no spectrum was observed.

Infrared studies of cyclobutene were difficult to undertake due to the large transmission losses (>60%) which accompanied adsorption of this compound, resulting from a release of electrons to the zinc oxide surface (*19*). Although the spectra were of poor quality they resembled very closely those obtained from 1,3-butadiene studies (*20*). While these studies did not yield convincing evidence for the formation of a π-allylic species, they suggested that ring opening was occurring through a strongly adsorbed π-bonded species. In addition, studies of cyclopentene indicated that the only surface species were probably strongly π-bonded species. Strongly adsorbed π-bonded species for cyclopentene are consistent with the observations of Smith and Ohlson (*15*) who studied silver nitrate–ethylene glycol as the liquid phase for gas chromatographic separation of olefins. They reported exceptionally large retention times for cyclopentene. Since retention times are directly related to the stability of the silver–olefin complexes, one would conclude that cyclopentene had formed a strong π-bonded complex (*21*). These results for zinc oxide are also consistent with the report by Chang and Kokes (*22*) who noted that this catalyst will not dissociate a carbon acid whose pK value is greater than 36. Since it has been found that the pK of cyclopentene is 44 (*23*), π-allylic formation by this compound should be improbable during adsorption on zinc oxide.

Isomerization of methylenecyclobutane was initially of interest as a comparison to that of cyclobutene and cyclopentene. Earlier studies had shown that during thermal isomerization methylenecyclobutane can react as such, with the ring intact or with cleavage of the ring, to yield linear molecules (*24*, *25*). In addition, isomerization over activated aluminas (*26*, *27*), aluminosilicates and synthetic zeolites (*28*), and sodium alumina (*29*) suggested that the compound was not very reactive. Over activated alumina (*26*, *27*), the authors found that isoprene was the major product at temperatures greater than 573°K. Studies over synthetic zeolites and natural and amorphous aluminosilicates (*27*) showed that products were dependent on the nature of the catalyst used. Methylenecyclobutane did not isomerize at temperatures below 473°K over NaA zeolites, but reaction at 473°K gave 1-methylcyclobutene as the sole product. At 523°K, 3-methylcyclobutene appeared in the reaction mixture but ring opening did not occur. With amorphous aluminosilicates, the sole product at 323°K was 1-methylcyclobutene, whereas, ring opening occurred at 423°K giving 2-methylbutenes. In comparison, Shabtai and Gil-Av (*29*) were able to produce 1-methylcyclobutene over finely divided sodium on alumina at 298°K. These combined observations tend to support the conclusion that basic catalysts would be more active for the isomerization of methylenecyclobutane. Hence, the infrared studies reported here will provide considerable insight into the mechanism for this reaction.

Figures 3 and 4 represent the spectra obtained during the adsorption of 0.0130 atm of methylenecyclobutane and after evacuation of the gas phase. (All spectra are divided into three regions of interest: OH stretching, CH stretching, and C–C stretching and CH deformation.) It is seen first that a new band appears in the OH stretching region at 3590 cm^{-1} which is indicative of the abstraction of an allylic hydrogen to form a π-allylic adsorbed species (*4*, *6*, *9*). In the CH stretching region the observation of the bands above 3000 cm^{-1} are characteristic of

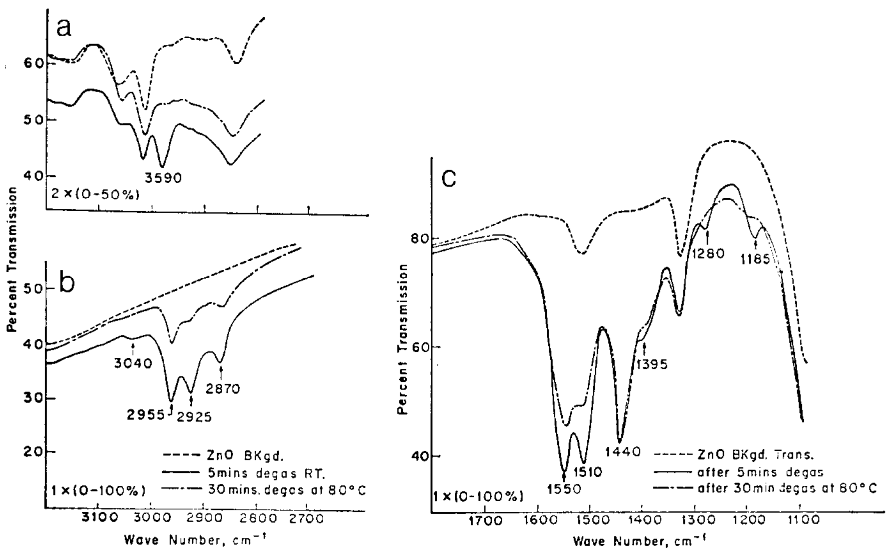


FIG. 4. Methylenecyclobutane on Kadox 25 zinc oxide infrared desorption study. (a) O–H stretching region; (b) C–H stretching region; (c) C–C stretching and C–H bending regions.

olefinic species on the surfaces. It must be noted that the band at 2925 cm^{-1} behaves somewhat differently with respect to time and degassing conditions than do the bands at 2955 and 2870 cm^{-1}. Note that the relative intensity of the 2925 cm^{-1} band is initially greater than that of the 2955 cm^{-1} band. However, upon degassing their intensities shift to the point that the 2955 cm^{-1} band becomes noticeably greater (30-min degassing at 353°K). This suggests that these two bands are due to different π-allylic species or to at least a combination of several surface species. Tentatively assigning the 2955 and 2870 cm^{-1} bands to methyl group vibrations suggests that such a surface species contains more methyl groups than methylene groups that can vibrate freely, i.e., not attached to the surface directly (*30*).

In the C–C stretching and CH deformation region the most important bands occur at 1640, 1550, and 1510 cm^{-1}. The band at 1640 cm^{-1} corresponds to a 45 cm^{-1} shift of the $\nu_{C=C}$ from its gas-phase position. Similar shifts have been reported for π-bonded ethylene (23 cm^{-1}), propylene (30 cm^{-1}), butene-1 (35 cm^{-1}) (*4, 8, 9*), and cyclopentene (50 cm^{-1}) (*20*). Since this band disappears on prolonged evacuation at room temperature or elevated temperature, it must be due to a weakly chemisorbed species. Thus, this band is assigned to a π-bonded methylenecyclobutane adsorbed on zinc oxide. See Fig. 6 for its proposed structure. (The negative band at 1680 cm^{-1} is due to the strong $\nu_{C=C}$ band in the gas phase and occurs because of an imbalance between the sample and reference cells caused by reaction of methylenecyclobutane to form 1-methylcyclobutene in the sample cell.)

Figures 3 and 4 show that the band at 1510 cm^{-1}, which is initially more intense than the band at 1550 cm^{-1}, decreases with time or with increasing degas temperature, whereas the band at 1550 cm^{-1} behaves in an opposite manner. Clearly, these two bands belong to different surface species. When these studies were repeated using 0.0065 atm of methylenecyclobutane in the gas phase, it was quite apparent that the 1510 cm^{-1} band was formed first (see Fig. 5). In addition, bands at 1550 and 1440 cm^{-1} formed much slower than in the 0.0130-atm case implying a pres-

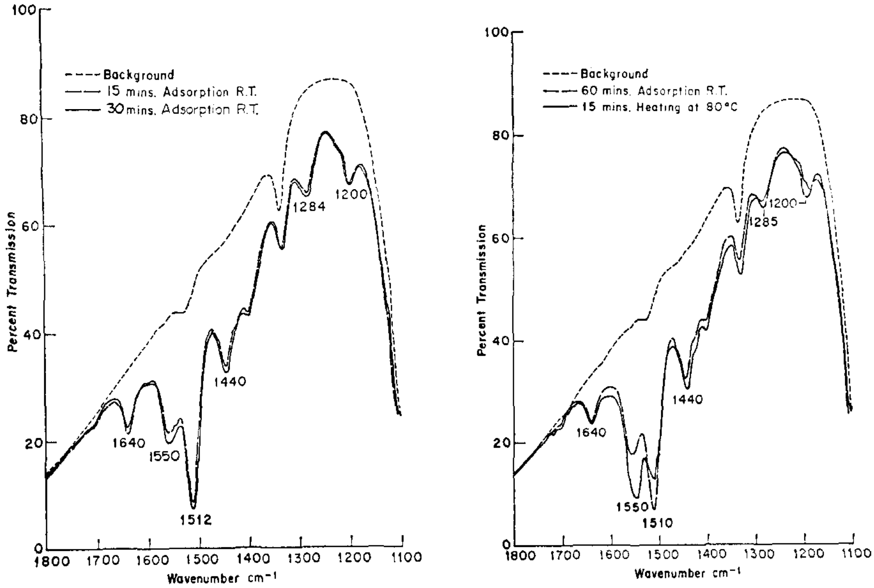


Fig. 5. Methylenecyclobutane on zinc oxide. Sample and reference-cell pressure = 0.0130 atm of 5% methylenecyclobutane in helium.

sure dependence on methylenecyclobutane. Thus, the 1510 cm^{-1} band has been assigned to the π-allylic species of methylene as shown in Fig. 6. It should be noted that this π-allylic species is also common to 1-methylcyclobutene and therefore, as indicated in Fig. 6, is the surface intermediate for the exo–endo isomerization of methylenecyclobutane to 1-methylcyclobutene.

The band at 1550 cm^{-1} is of interest; it is formed later than the band at 1510 cm^{-1}. This band increased slowly at room temperature, more rapidly at 353°K, but decreased in intensity as the cell was degassed at 353°K. In comparison, the 1510 cm^{-1} band formed rapidly at room temperature, increased rapidly at 353°K, but decreased *drastically* upon degassing at 353°K. When the integrated intensities of the bands from Fig. 5 and similar studies are plotted versus time, it becomes quite apparent from the slopes of band intensity–time curves that the 1640, 1550, 1510, and 1440 cm^{-1} bands all belong to different species. The species responsible for the 1550 cm^{-1} band appears to be formed after ring opening of an adsorbed methylenecyclobutane species. The nature of this band had been the subject of extensive ir studies to determine whether it is the π-allylic species that is the precursor of 1,4-pentadiene or 2-methyl-1,3-butadiene (isoprene).

In a separate isomerization study, a 7% of methylenecyclobutane in helium was circulated over 20 g of zinc oxide in the batch recycle reactor described in Fig. 2. After 30 min, the reaction was stopped by condensing the hydrocarbon products into a trap using liquid nitrogen. After degassing the helium, this material was transferred to a storage bulb for subsequent analysis. In addition, the material removed during degassing while heating the sample to 398°K (30 min) was collected in another bulb. Finally, the material removed by degassing from 398 to 673°K (30 min) was collected in a third bulb. Infrared and gas chromatographic analyses of these materials are summarized in Table 3. Although the evidence is not overwhelming by comparison of band intensities, it does appear that the bands assigned to the methyl vibrations (2955 and 2870 cm^{-1}) and the 1550 cm^{-1} band belong to the

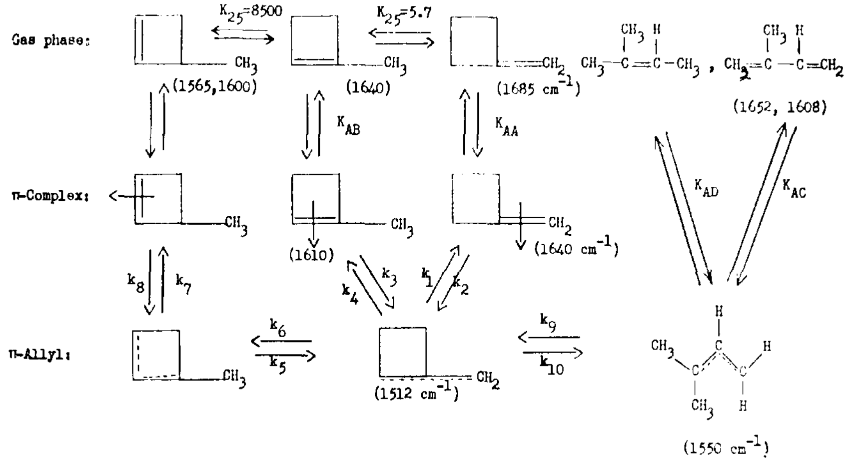


FIG. 6. Summary of catalytic adsorption of methylenecyclobutane on zinc oxide.

same species. Previous discussions implied that this species contained more methyl groups than methylene groups (*30*). Hence, the structure of this proposed π-allylic species is indicated in Fig. 6. Frey and Pope (*31*), Frey and Solly (*32*), and Dickens *et al.* (*33*) reported that in the ring-opening isomerization of 1-methylcyclobutene the major products was 2-methyl-1,3-butadiene which is additional supportive evidence. The 2-methyl-butene-2 which appears in the product mixture is probably formed by self-hydrogenation of 2-methyl-1,3-butadiene.

The band at 1440 cm^{-1} is also of interest, as it neither appears to be due completely to the π-allylic species nor to the π-bonded methylenecyclobutane. This band increased slowly with time or temperature of adsorption, but it is not decreased by prolonged evacuation at 398°K. While its assignment has not been completed, it is

TABLE 3

Summary of Isomerization Products for Methylenecyclobutane over Zinc Oxide[a,b]

Desorption temperature	Reaction product	Comments
Room temperature (298°K)	Methylenecyclobutane	Reactant
	1-Methylcyclobutene	Major product
	2-Methyl-2-butene[c]	Less than 2%
298–398°K	Methylenecyclobutane	Approximately equal amounts by gc
	1-Methylcyclobutene	
	2-Methyl-2-butene[c]	
	2-Methyl-1,3-butadiene[d]	Less than 5%
398–673°K	Methylenecyclobutane	Trace in gc analysis
	2-Methyl-1,3-butadiene	Major product as identified by gc and ir

[a] Gas chromatographic analysis was performed as described in the experimental section.

[b] Infrared spectra were obtained using a 10-cm path length cell at approximately 0.0130 atm on a Beckmann 4250 double-beam instrument.

[c] Found by gc only; this compound possibly could be 3-methyl-1-butene or a mixture of the two.

[d] This compound was identified in the gas chromatogram by estimating its retention time using the data of Smith and Ohlson (*15*). In addition, infrared spectra of this material strongly supported the gc conclusions.

probably associated with the material which remains on the zinc oxide surface after evacuation at 673°C.

Figure 6 summarizes the results of the infrared and adsorption studies of methylenecyclobutane on zinc oxide. The equilibrium constants were extracted from the work of Shabtai and Gil-Av (*29*). They show that the formation of 3-methylcyclobutane at low temperatures is thermodynamically unfavorable. The numbers in parentheses represent frequencies to the $\nu_{C=C}$ stretching band for the respective species. In this reaction pathway interconversion of methylenecyclobutane to 1-methylcyclobutene or isoprene is proposed to occur through the π-allylic species with $\nu_{C=C} = 1510\ cm^{-1}$. The π-complexed species serve as precursors. Based on preliminary infrared studies and an approximate 30 cm^{-1} shift we would anticipate that the π-bonded complex of 1-methylcyclobutene would adsorb at 1610 cm^{-1}. It is expected to be weak due to steric effects.

The π-allylic species common to methylenecyclobutane and 1-methylcyclobutene apparently slowly undergo a side reaction to produce the ring-opened π-allylic species which is common to 3-methyl-1-butene and 2-methyl-2-butene. The assignment solely to 2-methyl-2-butene may be fortuitous, but it reflects what others have found (*28*). Equilibrium isomerization studies (*20*) showed that less than 5% of the reaction products at temperatures between 298 and 373°K result in carbon skeleton rearrangement of the methylene cyclobutane during its isomerization to 1-methylcyclobutene. Our infrared studies confirm these results, but also suggest that the ring-opened π-allylic species is more strongly adsorbed, hence, its products escape less frequently into the gas phase. Additional work in this area is necessary to determine the rates in these side reactions, however.

Preliminary kinetic studies were undertaken to determine the activation energy for the isomerization of methylenecyclobutane. These studies were conducted at 299, 314, and 328°K at a partial pressure of 0.086 atm in helium, such that the total pressure was 1.108 atm. From the initial rates at low conversions, the apparent activation energy was found to be 14.0 ± 0.8 kcal/mol for the forward reaction and 15.2 ± 0.8 kcal/mol for the reverse. These data agree quite closely with those reported by Scriesheim and co-workers (*34*), who studied this reaction in a basic solvent made of potassium tert-butoxide and dimethylsulfoxide. For their base-catalyzed homogeneous reaction, they obtained an activation energy of 13.9 kcal/mol in the temperature range 298–328°K. Whereas Schriesheim *et al.* (*34*) considered the rate-determining step to be the abstraction of the allylic hydrogen, infrared studies in this work have shown that this step is very rapid and the rate-determining step appears to be the recombination of the adsorbed hydrogen with the π-allylic moiety.

In a final set of experiments, an attempt was made to observe the bands due to adsorbed hydrogen on zinc oxide (*4*, *5*, *17*) in the presence of the cyclo-olefins. In every case in which a mixture of the olefin in hydrogen or deuterium was exposed to a zinc oxide sample, no bands were observed which could be assigned to Zn–H or O–H vibrations. This also was the case when hydrogen was added to the preadsorbed olefin. However, when a 5% olefin in helium mixture was added to the ir cell containing preadsorbed deuterium, the infrared spectra indicated an immediate shift of the Zn–D band to successively lower frequencies, accompanied by a decrease in intensity until it completely disappeared. The rate of disappearance appeared to be diffusion limited (*20*). These results are typical of those observed for propylene and other olefins over zinc oxide (*4*, *6*) and reflect the mode of hydrogenation of these compounds (*10*). Since the hydrogen does not compete favorably for the available surface sites, hydrogenation is likely to occur via a Rideal–Hinchelwood-type mechanism (*10*).

The high reactivity of methylenecyclobutane compared to the low reactivity of cyclopentene over zinc oxide suggests that the two compounds isomerize by markedly different mechanisms. Hightower and Hall (*18*) reported that, over alumina, cyclopropane and cyclopentene underwent rapid izomerization reaction and deuterium exchange. This suggests that for these compounds the reactive surface intermediate has considerable carbonium ion characteristics, whereas for methylenecyclobutene the reactive surface intermediate has considerable carbonium characteristics (*22*). More importantly, the close agreement between the homogeneous base-catalyzed reaction and the heterogeneous reaction catalyzed by zinc oxide lends further support for emphasizing the similarity between the two systems.

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