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An Infrared Study of Isomerization of Acetylenes Over Zinc Oxide

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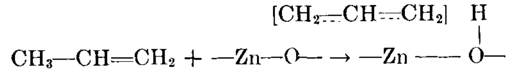
Absorbed acetylenes on zinc oxide are more strongly bound than the corresponding olefins, and, in contrast to olefins, the acetylenes are only partially desorbed, as such, even after degassing at 300°C. Addition of small amounts of acetylene gives rise to the immediate appearance of a band at 3550 cm^{-1}, a region characteristic of an OH bond, which suggests that dissociative adsorption occurs. Details of the spectrum of adsorbed acetylene and perdeuteroacetylene are consistent with this view. When a small amount of methyl acetylene is adsorbed, dissociative adsorption again occurs as indicated by the appearance of a band at 3515 cm^{-1}. Studies with labeled methyl acetylene, however, reveal that the initial dissociation occurs via removal of the methyl hydrogen to form a propargyl species. The propargyl species, also formed from allene, appears to function as an intermediate in allene–methyl acetylene isomerization.

INTRODUCTION

Infrared studies suggest that zinc oxide contains a limited number of pair sites which are capable of dissociatively adsorbing hydrogen (*1*, *2*) or olefins with allylic hydrogens (*3*, *4*). The process for olefins is represented as follows:



$$\mathrm{CH_3{-}CH{=}CH_2} + \mathrm{{-}Zn{-}O{-}} \rightarrow \overset{[\mathrm{CH_2 \cdots CH \cdots CH_2}]}{\mathrm{{-}Zn}} \;\text{-----}\; \overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}\mathrm{{-}}$$

where Zn–O represents the pair site and $[CH_2 \cdots CH \cdots CH_2]$ stands for a π-allyl species, which IR studies suggest is symmetric. Isomerization apparently occurs *via* a 1,3-hydrogen shift involving the allylic species as an intermediate. Inasmuch as the zinc and oxide ions of the active site are Lewis acids and bases, respectively, we can expect the allylic species to have anionic character and the abstracted hydrogen to have protonic character. Thus, the dissociative adsorption of propylene can be viewed as an acid–base reaction involving heterolytic fission of the most acidic carbon–hydrogen bond. Accordingly, we might expect that interactions of hydrocarbons with zinc oxide would resemble interactions of hydrocarbons with homogeneous bases (*5*). Recent studies of butene isomerization support this view insofar as the initial *cis/trans* ratio from 1-butene isomerization over zinc oxide shows the high value characteristic of isomerization via carbanions (*6*).

The nature of interaction of hydrocarbons with homogeneous bases is determined by the p*K* values of the hydrocarbon relative to that of the base. If, indeed, zinc oxide behaves as a base, one would expect a similar dependence of interaction pattern on the acidity of the hydrocarbon. Such an expectation carries with it the assumption that the interaction of surface cations with the carbanion is similar and/or nonspecific, e.g., is largely coulombic. For surface sites it would seem that such an assumption is, *in general*, an oversimplification. However, if we restrict our consideration to species similar in size and charge distributions, the surface–carbanion interaction may be sufficiently similar so that hydrocarbon acidity is the dominant factor. Acetylene and methyl acetylene are hydrocarbons similar in size to ethylene and propylene, but they are much more acidic (*7*). Just as olefins, in the presence of bases, isomerize via a 1,3 hydrogen shift of an allylic species, methyl acetylene in the presence of bases, undergoes isomerization to allene via a 1,3 hydrogen shift of a propargyl species (*7*). Thus, if the parallelism of zinc oxide to a homogeneous base catalyst is a valid one, studies of acetylenes (which are more acidic than olefins) should provide an interesting comparison to the published studies with olefins. A preliminary communication on this topic has appeared elsewhere (*8*).

EXPERIMENTAL METHODS

Catalysts and reagents. Zinc oxide used in these studies was Kadox-25 (New Jersey Zinc Co.). Unlabelled hydrocarbons (acetylene, methyl acetylene, and allene) were CP grade. Perdeuteroacetylene and 1-deuteropropyne were obtained from Merck. Hydrocarbons were purified by appropriate freezing, pumping and trap-to-trap distillation prior to use. The purity of labeled compounds was checked by IR analysis. The perdeuteroacetylene appeared to be isotopically pure, but the 1-deuteropropyne contained about 7% $\equiv$C—H.

Apparatus and procedures. Catalyst pretreatment was that described earlier (*3*). This yielded a catalyst with an area of 8–10 m^2/g. Procedures used for IR studies with a Perkin-Elmer 521 grating double beam spectrometer have been described elsewhere (*3*). All spectra were recorded at room temperature.

Adsorption measurements were carried out in a conventional BET apparatus with a 10 g sample of catalyst. Isomerization studies were carried out in an all-glass circulating system with a volume of about 140 cm^3 with an 11 g sample. All studies, unless otherwise specified, were carried out at room temperature.

RESULTS

Adsorption experiments. Admission of doses of acetylene to zinc oxide at room temperature shows adsorption is complete until more than 0.7 ml/g is admitted. Further dosing results in additional adsorption and the buildup of the gas phase pressure. The amount adsorbed, however, does not increase greatly with pressure; for example, at 11 mm 0.98 ml/g are adsorbed and, if the pressure is increased to 333 mm, the amount adsorbed increases to only 1.15 ml/g. A slow process accompanies adsorption as evidenced by the fact that desorption isotherms lie above adsorption isotherms. In a given adsorption–desorption run 1.07 ml/g remained after degassing at room temperature. Roughly 10% of this could be removed by evacuation at 300°C for a period of 1 hr. The remaining acetylene, or the residues thus formed, could be removed by burning in oxygen at 450°C. Similar adsorption characteristics were found for methyl acetylene. The irreversible adsorption was accompanied by a slow process; the amount irreversibly adsorbed at room temperature was about 0.7 ml/g and this chemisorbed species could not be removed as such even by degassing at 300°C. Thus, acetylenes are very strongly chemisorbed and at higher pressures may undergo surface reactions akin to polymerization.

Infrared studies on acetylenes. Figure 1 shows the spectrum of adsorbed acetylene in the OH and CH region as successive doses of acetylene (0.25 ml/g) are added to zinc oxide. The spectrum for several doses is not as well-defined as that for the initial doses. We shall assume that the loss of spectral features at higher coverages is the result of surface reaction and shall confine our discussion to the spectrum at low coverage which we feel is more characteristic of the strongly held acetylene. The band at 3550 cm^{-1} is clearly in the OH region and suggests dissociative adsorption occurs. Bands in the $\equiv$C—H region, however, are similar to those reported by Yates and Lucchesi (*9*) on alumina insofar as the lower frequency band (3230 cm^{-1}) is removed by evacuation at 80°C whereas the higher frequency band (3280 cm^{-1}) represents the more strongly held species. A band is also observed at 1975 cm^{-1}, a region corresponding

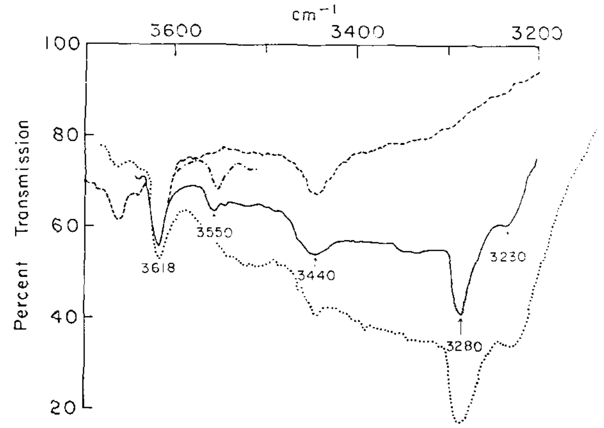


FIG. 1. Spectrum of chemisorbed HC≡CH on zinc oxide: background (- - -); first dose (- · -); second dose (——); third dose (. . .).

to a triple bond stretch, which is forbidden for gaseous actylene. Thus, it appears that acetylene adsorbs dissociatively on zinc oxide to form an OH and a surface acetylide.

In the absence of other data it may be argued that the band at 3550 cm^{-1} represents a hydrogen bonding distortion of the surface hydroxyl bands rather than dissociative adsorption. Figure 2, which shows the spectrum of perdeuteroacetylene on zinc oxide, makes this interpretation unlikely. We find no band in the OH region when C_2D_2 is adsorbed but we do observe several bands in the OD region. Bands are evident in spectra d and e at 2667, 2622 and 2550 cm^{-1} (in addition to those characteristic of ≡C—D vibrations). Bands at 2700, 2686, 2667 and 2550 cm^{-1} correspond to those observed for a surface in which the surface hydroxyls have been changed to deuteroxyls by exchange (spectrum f). If the 3550 cm^{-1} band observed with C_2H_2 undergoes a similar isotope shift, we would expect it to appear at 2623 cm^{-1}. The appearance of a band at 2622 cm^{-1} on adsorption of C_2D_2 even when the surface deuteroxyl concentration is low (spectrum d) is strong support for the view that this band forms by dissociative adsorption. Bands at 2667 and 2550 cm^{-1} suggest that the C_2D_2 exchanges readily with surface hydroxyls but the latter may stem in part from a ≡C—D vibration. [As before (*3*) we shall use the term hydroxyl or deuteroxyl to describe background bands; the term OH or OD band will be used to describe species formed by dissociative adsorption.]

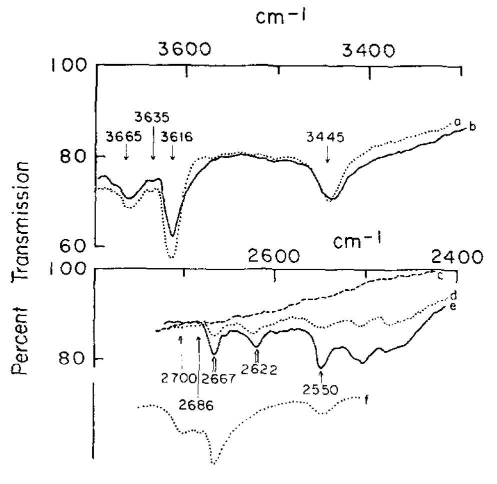


FIG. 2. Spectrum of chemisorbed DC≡CD on zinc oxide: background (a) and (c); first dose (b) and (d); second dose (e); background deuteroxyls (f).

Figure 3 (spectrum c) and Fig. 4 (solid line) show the spectrum of adsorbed methyl acetylene. Once again, the spectrum shows a band in the OH region (at 3515 cm^{-1}) which suggests dissociation occurs. A broad band is also observed at 3250 cm^{-1}, which is below the ≡C—H band for gaseous methyl acetylene (*10*) (3334 cm^{-1}) but suggests a ≡C—H is still present and

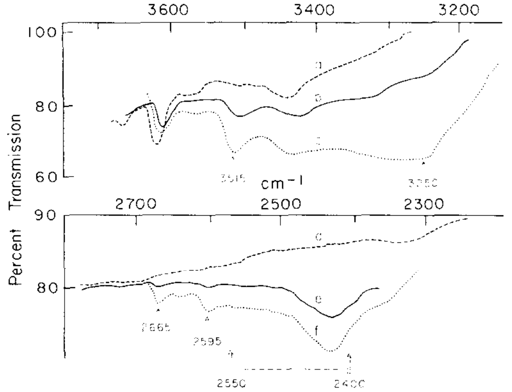


FIG. 3. Spectrum of chemisorbed propyne on zinc oxide: background (a) and (d); second dose of $CH_3C\equiv CH$ (c); second dose of $CH_3—C\equiv C—D$ (b) and (e); third dose of $CH_3—C\equiv C—D$ (f). Arrows connected by broken line correspond to expected region for $\equiv C—D$.

that the dissociation is not due to the acetylenic hydrogen. Other observed bands are listed in Table 1 along with fundamentals and strong overtones for similar gas-phase molecules. The spectrum of adsorbed $CH_3—C\equiv C—D$ is also shown in Fig. 3 (spectra b, e and f). Initially strong bands appear at 3515 and 2425 cm^{-1}; *the former is clearly an OH band* and the latter falls within the expected range (see later) for the $\equiv C—D$ band. Thus, consistent with the observations with $CH_3—C\equiv C—H$, it appears that a methyl hydrogen is abstracted and bound by the oxygen and the acetylenic hydrogen remains largely intact. When larger doses of $CH_3—C\equiv C—D$ are admitted or, at later times, a band appears at 2665 cm^{-1} indicating hydroxyl exchange with the acetylenic deuterium. Also under these conditions a band appears at 2595 cm^{-1}. This latter band does not correspond to a deuteroxyl

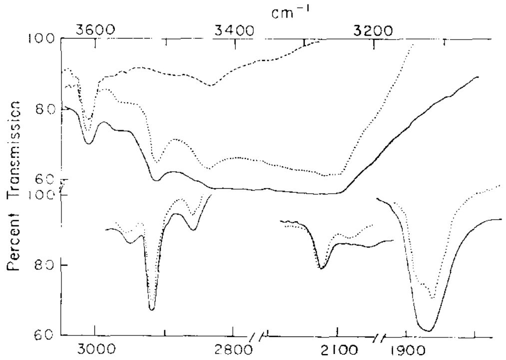


FIG. 4. Spectrum of chemisorbed allene and propyne on zinc oxide: background (– – –); allene (. . .); propyne (displaced ordinate) (——).

TABLE 1
BAND POSITIONS (cm^{-1}) FOR GASEOUS METHYL ACETYLENE AND ALLENE, AND ADSORBED METHYL ACETYLENE

$CH_3—C\equiv CH(g)$(*10*)	$CH_2=C=CH_2(g)$(*11*)	$CH_3—C\equiv CH$(ads)
		3515 m
3334 vs		3250 br vs
	3085[b]	
3008 m	3005 m	2950[c] w
2941 vs	2996[b]	2920 s
2881[a] m		2855 w
2142 m	2015[a] w	2120 w
		2080 vw
	1957 vs	1865 vs
	1680[a] m	
1452 s	1440[b]	(1440)[d] vw
1382 w	1398 w	(1370)[d] vw

[a] Strong overtone.

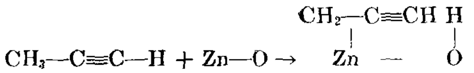
[b] Forbidden in gas phase.

[c] This band seems to grow more with successive doses than other bands in this region.

[d] These bands are evident only in the presence of gaseous methyl acetylene; hence, they may be due to a physically adsorbed species.

position but does correspond closely to the expected position (2598 cm^{-1}) of the isotope shifted 3515 cm^{-1} band. At coverages where this band forms, however, a band also forms at 3250 cm^{-1}, which suggests that the OD band is, in part, a result of an "isomerization" of the labelled methyl acetylene.

By analogy to the results with propylene we might expect the dissociative adsorption by hydrogen abstraction from the methyl group of propyne to occur as follows:



$$CH_3{-}C{\equiv}C{-}H + Zn{-}O \rightarrow \begin{array}{cc} CH_2{-}C{\equiv}CH & H \\ | & | \\ Zn \quad - & O \end{array}$$

If, however, the hydrocarbon fragment is essentially a propargyl anion $[CH_2{-}C{\equiv}CH]^-$, there are two resonance forms for the resulting resonance hybrid:

$$\bar{C}H_2{-}C{\equiv}CH \leftrightarrow CH_2{=}C{=}\bar{C}{-}H$$

Then one might expect that the spectrum of adsorbed methyl acetylene would be essentially the same as that of allene. Figure 4 compares the spectrum of adsorbed methyl acetylene (solid line) to that of allene (dotted line) under closely similar conditions. The bands are not quite as sharply structured for methyl acetylene but the spectra are, indeed, nearly identical. Moreover, the comparison in Table 1 shows the spectrum of the adsorbed species shows little resemblance to either of the parent molecules.

Kinetic studies. The IR adsorption studies suggest zinc oxide should be an effective catalyst for allene–methyl acetylene isomerization; hence, we have examined this catalytic reaction in a circulating system. Zinc oxide is, indeed, a catalyst; at room temperature circulation of 14 ml of allene over 11 g of catalyst gives 90% gas-phase conversion in about 3 hr (about 8 ml are adsorbed by the catalyst). The kinetics for the first half of the reaction can be represented fairly well by a first order plot in the distance from equilibrium but the rate becomes progressively slower than this in the latter stages of the reaction. (For 300°K the equilibrium yield of methyl acetylene is 96% (*11*).) Departure from this relationship sets in earlier at higher pressures. Such plots for pressures ranging from 40 to 200 mm yield initial rates of the order of 5×10^{10} molecules/sec/cm^2. Since poisoning was evident during the course of the reaction and the study was cursory, we regard this value as a rough estimate but it is probably accurate within a factor of 2.

Details of the IR spectrum provide additional information on the course of this reaction. Figure 5 compares the spectra for small doses of propyne and 1-deuteropropyne below 3000 cm^{-1} under comparable conditions. The spectra shown are those obtained in scans started at higher frequencies immediately after admission of the gas; for the lowest frequencies the spectra were obtained about 15 min after admission of the gas. The spectra in Fig. 5 are quite similar except in the region between 1800 and 1900 cm^{-1}. Here propyne yields a single slightly asymmetric band at 1865 cm^{-1}. The labeled propyne, however, shows two bands: The higher frequency band (1865 cm^{-1}) is asymmetric and, in area, is two to three times as intense as the lower frequency band (1830 cm^{-1}). If this region of the spectrum is scanned immediately after addition of 1-deuteropropyne, we find that in the first

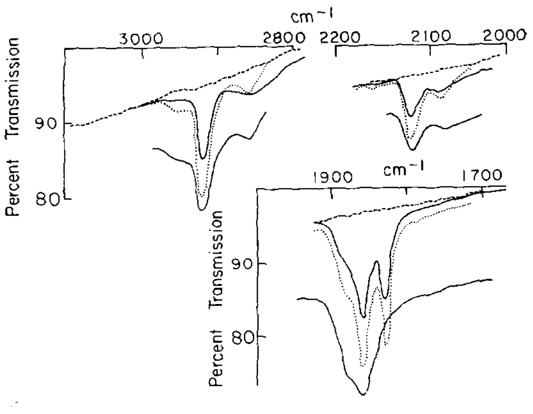
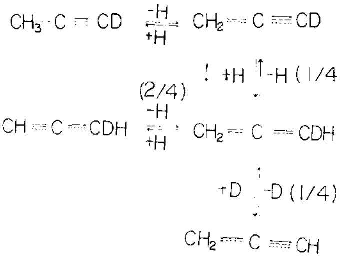


FIG. 5. Spectrum of chemisorbed $CH_3C{\equiv}CD$ and $CH_3C{\equiv}CH$ on zinc oxide: background (- - -); second dose $CH_3{-}C{\equiv}CD$ (——); third dose $CH_3{-}C{\equiv}CD$ (. . .); second dose of $CH_3{-}C{\equiv}CH$ (——) (displaced ordinate).

scan, only the 1830 cm^{-1} band is evident. Repeated scans in this region reveal that the 1865 cm^{-1} appears shortly and reaches an intensity equal to that of the 1830 cm^{-1} band in 2 to 3 min. After about 6 min the relative intensity of these two bands is comparable to that shown in Fig. 5. Thus, it is clear that there is a rapid process accompanying adsorption of the labeled propyne that is not evident for the unlabeled propyne.

Consider the origin of the 1865 cm^{-1} band in adsorbed methyl acetylene. If a propargyl ion is formed, we would expect a band in this region from the $C\underset{\cdots}{=}C$ stretch. If we assume the hydrogen bound to the terminal carbon moves with it and the $C\underset{\cdots}{-}C$ bond is so soft that it is decoupled from this vibration, the reduced mass for this vibration is 6.24 amu. On this basis when deuterium is bound to the end carbon, the reduced mass becomes 6.46 and we would expect a frequency shift by a factor of $(6.22/6.48)^{1/2}$, i.e., to 1833 cm^{-1}, which is very close to the band position observed initially for 1-deuteropropyne. When deuteropropyne is adsorbed, we would expect the following to occur:



In the absence of an isotope effect the fractions in parentheses represent the relative probabilities of hydrogen (or deuterium) removal from the allene to form the indicated species.) On this basis, on adsorption of the labeled propyne the species $CH_2\underset{\cdots}{-}C\underset{\cdots}{=}CD$ (with a band at 1830 cm^{-1}) should form first; in time, however, the species, $CH_2\underset{\cdots}{-}C\underset{\cdots}{=}CH$ or $CHD\underset{\cdots}{-}C\underset{\cdots}{=}CH$ (with a band at 1865 cm^{-1}) forms; finally, at equilibrium, the latter species should be predominant by a factor of 3 to 1 in the absence of an isotope effect. This is in good agreement with the observed results.

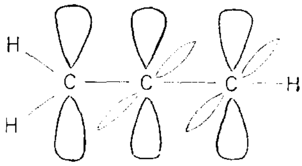
If, indeed, isotope effects are absent, the rate of appearance of the 1865 cm^{-1} band from labeled propyne provides a measure of the rate of the 1,3 hydrogen shift. For a dose of 0.4 ml/g it takes about 2 min for the 1865 cm^{-1} band to become as intense as the 1830 cm^{-1} band. This implies a rate of the order of 0.1 ml/min per g of catalyst or 8×10^{11} molecules/sec/cm^2. Thus, the rate of the 1,3 shift appears to be at least an order of magnitude faster than the isomerization rate (5×10^{10} molecules/sec/cm^2).

DISCUSSION

The resonance structure of the propargyl ion is as follows:

$$\bar{C}H_2-C\equiv CH \longleftrightarrow CH_2=C=\bar{C}H$$

As written, the two forms imply different nuclear geometries; for resonance, we must have a common compromise geometry. One attractive geometry is that in which the $-CH_2$ group has sp^2 σ bonds and the C–C–H group has sp σ bonds. This leads to the following structure:

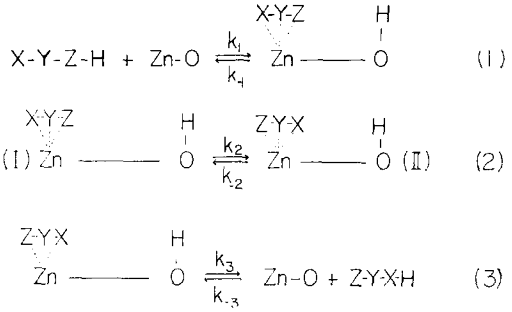


wherein the planar molecule has three overlapping p orbitals above and below the plane and the CH_2 group interacts by hyperconjugation with the remaining p orbitals. These two effects may lead to considerable resonance stabilization. The resulting species is quite similar to the π-allyl and it would seem that the propargyl species, like the π-allyl, would lie flat on the surface and bond via its three p orbitals.

Detailed band assignments for adsorbed methyl acetylene (see Table 1) are uncertain for two reasons: (1) There is evidence of surface reactions at higher pressures; hence, the observed spectrum, even in dosing experiments may stem from more than one species. (2) Coupling of group frequencies is pronounced for linear or near linear molecules; hence, group frequencies may undergo unexpectedly large shifts for the propargyl species. This second factor is quite evident even for gaseous perdeuteropropyne inasmuch as (apparently) C–D coupling with C$\equiv$C makes the former unexpectedly high and the latter unexpectedly low. Despite this uncertainty, we have made the following tentative assignments for stretching frequencies of the propargyl ion: $\overset{\cdots}{=}$CH, 3250 cm^{-1}; $\overset{\cdots}{-}CH_2$ 2920, 2855 cm^{-1}, and C$\overset{\cdots}{=}$C, 1865 cm^{-1}. For such an assignment to be reasonable we must assume strong coupling of CH stretches. The bands at 2950, 1440, and 1370 cm^{-1} are too pressure sensitive to be assigned to the dissociatively adsorbed species; hence, we assume that no bending frequencies assignable to the propargyl species are observed. The bands at 2120 and 2080 cm^{-1}, however, do correspond to strongly held species and appear for both labeled and unlabeled propyne. They may represent a side reaction to form methyl acetylide (similar to acetylene) but this reaction occurs to such a limited extent that no corresponding OH (or OD) is detected.

There are two features of the bands assigned to $\overset{\cdots}{=}$C—H (or $\overset{\cdots}{=}$C—D) that merit special comment. First, one would expect the growth of the 1865 cm^{-1} band and the relative decline of the 1830 cm^{-1} band for 1-deuteropropyne to be paralleled by a growth in the 3250 cm^{-1} ($\overset{\cdots}{=}$CH) band and a relative decline in the 2425 cm^{-1} ($\overset{\cdots}{=}$CD) band. Qualitatively, this is found; quantitatively, the growths and declines are not strictly parallel and, hence, other species may contribute to these $\overset{\cdots}{=}$C—H bands. Second, the ratio of the frequency for $\equiv$C—H compared to $\equiv$C—D in *gaseous* methyl acetylene is 1.27; presumably the small isotope shift stems from coupling of the $\equiv$C—D stretch with the nearby triple bond stretch. For the *peak* $\overset{\cdots}{=}$CH (and $\overset{\cdots}{=}$CD) frequencies for *adsorbed* species the ratio is 1.34; this more normal isotope shift suggests that coupling effects are less, as would be expected if on adsorption the full triple bond is weakened. In sum, then, the assignment, although it has some deficiencies, provides a reasonable basis for assuming that the adsorbed species is, at least in part, a propargyl species.

The evidence suggests that over zinc oxide both double bond isomerization and methyl acetylene isomerization occur via a 1,3 hydrogen shift. In terms of the picture that the active site acts like an acid–base pair site, we can represent this sequence schematically as follows:



The first step represents dissociative adsorption. The second step represents the surface rearrangement which is a necessary prelude to readdition of hydrogen on a different carbon atom; this step may involve rotation of the X–Y–Z fragment about an axis perpendicular to the surface or migration of the hydrogen atom. The last step represents readdition of the hydrogen atom and desorption of the product. The initial rate when the back reaction is negligible is given by

$$\frac{d[\mathrm{ZYXH}]}{dt} = k_3[\mathrm{II}]. \tag{4}$$

When a steady state is established for II (and I) this initial rate expression becomes

$$\text{Rate} = \frac{k_3k_2k_1P}{k_1P(k_2+k_{-2}+k_3)+k_{-1}(k_{-2}+k_3)+k_3k_2}, \tag{5}$$

where P is the pressure of reactant. If, indeed, the reaction pathway resembles that for similar reactions with homogeneous base catalysts, the rate constants should change to reflect changes in the effective hydrocarbon acidity. Figure 6 depicts how we would expect these rate constants to vary as a function of the acidity of the hydrocarbon. In drawing these curves we

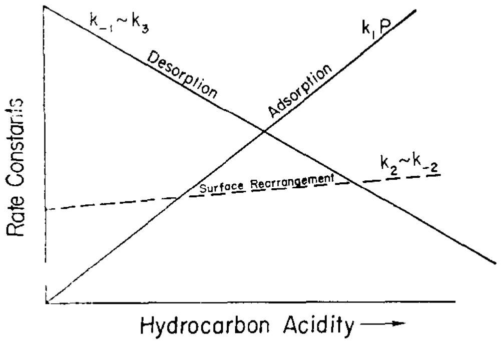


FIG. 6. Effect of hydrocarbon acidity on rates of elementary steps (schematic).

have assumed for simplicity that the gaseous and adsorbed reactants and products have similar stability and that the adsorption-desorption rate constants reflect the acid-base nature of the reaction. It is difficult to predict the variation of rate constants k_2 and k_{-2} with hydrocarbon acidity. If the mobility of the hydrogen governs the rate, k_2 and k_{-2} may be nearly independent of hydrocarbon acidity; if rotation of the anion governs the rate, the constants k_2 and k_{-2} may increase with anion stability, i.e., with hydrocarbon acidity. As a compromise between these views, we have indicated that the surface migration rate constant increases only slowly with hydrocarbon acidity. In this approximation there are three limiting forms for Eq. (5). When the hydrocarbon acidity is low k_3, $k_{-1} > k_2$, $k_{-2} > k_1P$ and we obtain

$$\text{Rate} \cong \frac{k_3k_2k_1P}{k_{-1}(k_2+k_3)+k_3k_2} \cong k_2\frac{k_1}{k_{-1}}P. \quad (6)$$

In this regime adsorption of reactants is at equilibrium in the Henry's law region, the isomerization rate is first order in the pressure of reactants and is equal to the rate of the surface rearrangement. For intermediate hydrocarbon acidity, $k_1P > k_{-1}$, $k_3 > k_2$, k_{-2} and we obtain

$$\text{Rate} = \frac{k_3k_2k_1P}{k_1P(k_2+k_{-2}+k_3)} \cong k_2. \quad (7)$$

In this regime the surface is nearly covered with I, the isomerization rate is zero order in the pressure of reactants and is equal to the rate of surface rearrangement. For very high hydrocarbon acidity $k_1P > k_2$, $k_{-2} > k_{-1}$, k_3 and we obtain

$$\text{Rate} = k_3\frac{k_2}{k_2+k_{-2}+k_3} \cong k_3\frac{k_2}{k_2+k_{-2}}. \quad (8)$$

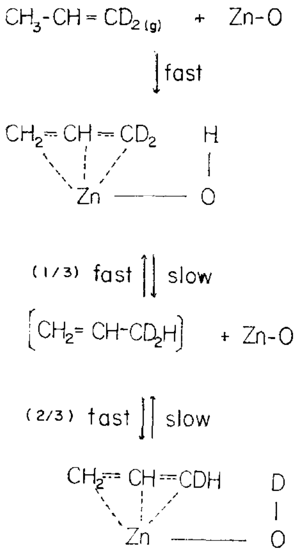
In this region the surface is covered with I and II, and the isomerization rate is zero order in the pressure of reactants and equal to the rate of desorption of II present in proportions established by an equilibrium for step 2. Under these conditions the catalytic isomerization rate is slower than the surface rearrangement rate.

Consider first double bond isomerization. Earlier studies (*3*) showed that catalytic "isomerization" of $CH_3—CH=CD_2$ occurred in the sequence:

$$CH_3—CH=CD_2 \rightarrow CH_2=CH—CD_2H \rightarrow CH_2D—CH=CDH. \quad (9)$$

Kinetics were not determined but the initial rate of isomerization of butenes is zero order (*6*). If we assume zero order kinetics also obtains for propylene, the overall rate of isomerization would be 3.7×10^{10} molecules/sec/cm^2. The rate of the 1,3 hydrogen shift was studied by IR techniques. Adsorption of $CH_3—CH=CD_2$ is fast and the spectrum reveals the immediate appearance of an OH band. Even in the absence of gas phase and weakly held (π-bonded) propylene, a slow surface process occurs in which (among other things) the intensity of the OH band declines and an OD band appears and increases in intensity. The OH and OD bands appear to approach an equilibrium wherein the amount of OH falls to 60% of its initial value and the OD approaches a concentration equal to 40% of the initial OH concentration. This is consistent with the following sequence:

wherein the species in brackets corresponds to an adsorbed species not directly observed. Since readsorption of the bracketted species is presumed to be fast, the rate of appearance of OD provides a measure of the 1,3 hydrogen shift on the surface. If we assume the band intensity after 7 hr represents equilibrium, the half time for approach to equilibrium (based on OH)



is 40 min. With the assumption that approach to equilibrium is first order, this yields a rate of 2.9×10^{10} molecules/sec/cm^2. In the absence of an isotope effect, the rate of 1,3 transfer would be 3/2 of this value. Thus, the estimated rate of surface rearrangement, 4.3×10^{10} molecules/sec/cm^2, is essentially the same as the estimated overall catalytic rate of double bond isomerization.

Let us now compare the results for olefin isomerization with the results for isomerization of the more acidic acetylenes. For olefins the isomerization rate appears to be zero order and equal to the rate of surface rearrangement. In terms of the steady state analysis, this conforms to the regime for hydrocarbons with intermediate acidity [Eq. (7)]. For the acetylenes, however, the catalytic rate (5×10^{10} molecules/sec/cm^2), which is roughly zero order, is less than the rate of surface rearrangement (8×10^{11} molecules/sec/cm^2), a result which puts acetylenes in the regime characteristic of high hydrocarbon acidity with product desorption as the rate controlling step. Thus, this comparison yields a familiar picture [one containing the principal features of "Ballandin's volcano" (*12*)] and suggests that the view that zinc oxide behaves like a basic catalyst may have some predictive value.

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REFERENCES

1. Eischens, R. P., Pliskin, W. A., and Low, M. J. D., *J. Catal.* **1,** 180 (1962).

2. Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **73,** 3772, 3781 (1969).

3. Dent, A. L., and Kokes, R. J., *J. Amer. Chem. Soc.* **92,** 6709, 6718 (1970).

4. Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **75,** 487 (1971).

5. Bank, S., Schriesheim, A., and Rowe, C. A., Jr., *J. Amer. Chem. Soc.* **87,** 3224 (1965).

6. Conner, W. C., and Kokes, R. J., unpublished data.

7. Iwai, I., *in* "Mechanisms of Molecular Migrations" (B. S. Thyagarajan, Ed.), Vol. 2, p. 13. Wiley, New York, 1969.

8. Chang, C. C., and Kokes, R. J., *J. Amer. Chem. Soc.* **92,** 7517 (1970).

9. Yates, D. J. C., and Lucchesi, P. J., *J. Chem. Phys.* **35,** 243 (1961).

10. Boyd, D. R. J., and Thompson, H. W., *Trans. Faraday Soc.* **48,** 493 (1952).

11. Lord, R. C., and Venkateswarlu, P., *J. Chem. Phys.* **20,** 1237 (1952).

12. Rootsaert, W. J. M., and Sachtler, W. M. H., *Z. Phys. Chem. (Frankfurt am Main)* **26,** 16 (1960).