

Characterization of Adsorbed Intermediates on Zinc Oxide by Infrared Spectroscopy

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All studies of rates of reaction have as their goal the answer to one or all of the following questions: (1) what are the reacting species; (2) what are the intermediate species; (3) what are the atom-by-atom motions that define the pathway of reaction? Ideally, the best kinds of answers emphasize structural detail, and if such answers are obtained, we can truly say that the reaction is "well-defined." The catalog of such "well-defined" reactions is brief, but the entries for homogeneous systems far outweigh those for heterogeneous systems. Why has the stated goal been more elusive for heterogeneous systems?

Mechanistic studies of homogeneous reaction rates rely heavily on rate laws. These laws, interpreted in terms of pseudoequilibrium of thermodynamically ideal or regular systems, have been central to elucidation of rate processes. In recent decades the availability of isotopes and the development of instrumental techniques have expanded the horizons of kineticists, but the rate law and its analysis are still central to reaction rate studies. This happy circumstance is possible only because the basis of rate law interpretation, *i.e.*, pseudoequilibrium of thermodynamically ideal or regular systems, is at least roughly approximated for homogeneous systems. The utility of rate laws for heterogeneous systems is not nearly as great. Few systems follow thermodynamically ideal, *i.e.*, Langmuir, or regular, *e.g.*, Freundlich, behavior for gas-solid equilibrium, under reaction conditions. Accordingly, *except for limiting cases*, rate laws based on gas pressures (or solution concentrations) are less useful for heterogeneous systems than for homogeneous systems.

In principle, it could be possible to obviate this problem by obtaining rate expressions in terms of the total surface coverage, θ . Unfortunately, it is well established that many surfaces are energetically heterogeneous so that surface species have a broad spectrum of reactivity; in effect, this means that deviations from ideality are very great and the interpretation of rate laws on the usual basis is not clear-cut. Thus, studies of heterogeneous catalysis are severely hampered by the fact that one of the most powerful tools available for homogeneous systems, that is, the rate law with its interpretation, is largely ineffective for heterogeneous systems.

The above conclusion would be devastating if the rate law and related concepts were the ultimate goal

of kinetic studies, but the rate law formulation is just a means to the end. To achieve the stated goals, all we need is an effective instrumental technique for determining the structure and reaction pathway of surface species on catalysts in their usual form (powders) at pressures of reactants (*e.g.*, 1 atm) normally encountered in catalytic reactions. Furthermore, this technique should be generally applicable to most of the molecules of interest. Unfortunately, many instrumental techniques (*e.g.*, high-resolution nmr) were developed for homogeneous systems and are not readily adaptable for studies of heterogeneous systems. Some are applicable to powders, *e.g.*, esr or Mössbauer spectroscopy, but are limited to certain kinds of catalysts or adsorbed species. Still others are ideal for structural studies of surface species, *e.g.*, low-energy electron diffraction or ESCA, but are either unusable with powders or require such low gas pressures (10^{-8} to 10^{-4} mm) that extrapolation to the usual catalytic conditions (10 to 10^3 mm) is at best courageous.

Infrared spectroscopy of adsorbed species, pioneered by Eischens and coworkers,¹ represents to us the technique most closely satisfying the requirements of broad applicability under common catalytic conditions. It suffers from the fact that structural analysis is not as clear-cut as with other techniques, but this difficulty can be offset in part by liberal use of labeled compounds and by close coupling of the ir studies to traditional mechanistic studies.

A happy marriage of infrared to traditional catalytic studies cannot always be effected. It is most promising when subsidiary experiments show the adsorption process is simple enough so that interpretation of the spectrum of the adsorbed species is feasible. Consider, for example, adsorption of ethylene on nickel hydrogenation catalysts. When the clean metal is exposed to ethylene, some adsorbs to form the reactive precursor of the ethane product and some undergoes a surface reaction to form relatively inert residues corresponding roughly to adsorbed acetylene and/or dimeric species.¹ Even though these residues are inert, they do respond to a hydrogen atmosphere.² Since the infrared spectrum sees all these species, it is not easy to pick out that part of the spectrum due to the reacting species.

By way of contrast zinc oxide is a catalyst for which ethylene adsorption occurs without troublesome side reactions.^{3,4} This catalyst also has excel-

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

(2) J. P. Bartek, Ph.D. Thesis, The John Hopkins University, 1970.

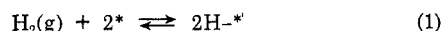
(3) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, 73, 3772, 3781 (1969).

(4) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, 74, 3653 (1970).

lent ir transmission between 4000 and 1100 cm^{-1} . Because it is much less active than metals, it is possible to follow reactions of interest at room temperature on a time scale compatible with that required for repeated ir scans.

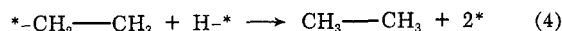
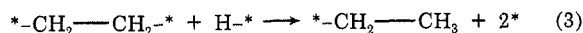
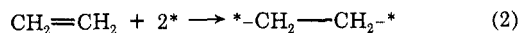
Accordingly, we have chosen zinc oxide for study and shall confine our discussion to the adsorbed species and intermediates that play a role in olefin hydrogenation and related reactions over this catalyst. Since we wish to emphasize the use of ir techniques to study the reaction sequence in catalysis, we shall, except in the simplest cases, simply quote the published structural assignments for adsorbed species. We wish to emphasize, however, that with the liberal use of deuterium labeling structural assignments for adsorbed organic molecules can be made with reasonable precision. Readers interested in this aspect of these studies should refer to the work on propylene⁵ which we consider our best example.

Hydrogenation of Olefins. A critical step in olefin hydrogenation is "activation" of hydrogen. By activation we mean provision of a pathway for facile rupture of the hydrogen-hydrogen bond. Once this is done, the reaction proceeds readily. For example, although the uncatalyzed reaction of *molecular* hydrogen with olefins is inappreciable below 800°K,⁶ the uncatalyzed reaction with *atomic* hydrogen is rapid even at 80°K.⁷ Catalysts which effect hydrogenation of ethylene usually also effect hydrogen-deuterium exchange, a reaction which occurs in the gas phase (at about 1000°K) *via* hydrogen atoms.⁸ Catalysis of the exchange reaction can be ascribed to the reversible reaction of molecular hydrogen with the dangling bonds at the surface (eq 1, where * represents a



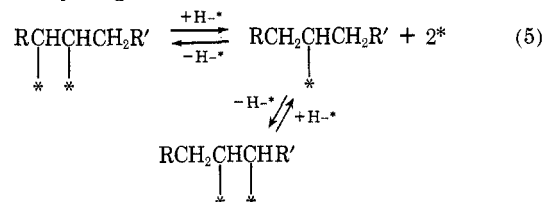
surface atom, followed by random recombination of the adsorbed atoms). (In some cases, however, the exchange is ascribed to reaction of the adsorbed atoms with molecular hydrogen.) The exchange reaction, like the catalyzed hydrogenation, will occur at temperatures as low as 100°K over catalysts such as nickel.⁹

Most of the studies of olefin hydrogenation have been carried out with reduced metal catalysts; hence, we consider first the observations for metals.¹⁰ For these, the reaction sequence probably involves adsorption of ethylene (with opening of the double bond to form a paraffinic species¹) followed by stepwise addition of adsorbed hydrogen atoms, *viz.*



Use of deuterium rather than hydrogen leads to eth-

ane products of the form $\text{C}_2\text{H}_6-x\text{D}_x$ ($0 \leq x \leq 6$) and exchange with the ethylene. Since exchange of deuterium with ethane is not rapid under mild conditions, the observation of the isotopic smear in the ethanes coupled with observation of ethylene and $\text{H}_2\text{-D}_2$ exchange suggests that steps 1 through 3 are reversible but that step 4 is irreversible and rate controlling. The ready reversibility of steps 2 and 3 provides a mechanism for the double bond isomerization that accompanies hydrogenation of higher olefins.¹⁰ This can be represented in terms of adsorbed olefins as in eq 5. Hydrogen should be a required cocatalyst



for isomerization *via* this pathway, and, in fact, under mild reaction conditions, the reaction is faster by several orders of magnitude in the presence of hydrogen.² Thus, the reverse of step 3, *i.e.*, alkyl reversal, is an important aspect of both hydrogenation and isomerization catalysis over metals.

Metal oxides¹¹⁻¹³ also effect both hydrogenation and isomerization. Like the metals, they also effect hydrogen-deuterium exchange;¹⁴ hence, they "activate" hydrogen in the same sense metals do. Hydrogenation is likely to proceed *via* the same sequence, but there is one important difference. Addition of deuterium to ethylene leads to essentially pure $\text{CH}_2\text{DCH}_2\text{D}$, and there is no exchange of the ethylenes. Thus, alkyl reversal is not a significant component of hydrogenation. If alkyl reversal does not occur readily, we must look for an alternative mechanism for isomerization.

Hydrogen Activation over Zinc Oxide. If one exposes an activated sample of zinc oxide to hydrogen at room temperature, there is a rapid adsorption of hydrogen followed by a slower process. This adsorbed hydrogen adsorption can be separated into two types. The first, type I, is rapid and reversible; the second, type II, is irreversible and, although some of this occurs rapidly, it is the major component of the slow hydrogen chemisorption. Tracer experiments, at or near room temperature, have shown that type II hydrogen is inert in ethylene hydrogenation and hydrogen-deuterium exchange, but that type I hydrogen participates in both of these reactions.^{15,16} Selective adsorption experiments show that the sites for type I adsorption constitute only a fraction of the surface (5-10%) and that, when these are blocked out by the selective adsorption of water, reaction is poisoned. Thus, it appears that the sites for type I hydrogen adsorption are those responsible for hydrogen activation and, hence, these are the active sites for these reactions.

(5) A. L. Dent and R. J. Kokes, *J. Amer. Chem. Soc.*, **92**, 1092, 6709 (1970).

(6) J. Aigueperse and S. J. Teichner, *J. Catal.*, **2**, 359 (1963).

(7) R. D. Gonzalez and R. J. Kokes, *J. Phys. Chem.*, **70**, 2535 (1966).

(8) H. S. Johnston, "Gas Phase Reaction Rate Theory," The Ronald Press, New York, N. Y., 1966, Chapter 10.

(9) For a discussion of hydrogen activation, see "Catalysis," Volume III, P. H. Emmett, Ed., Reinhold, New York, N. Y., 1955: (a) B. M. Trapnell, Chapter I; (b) D. D. Eley, Chapter II.

(10) G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962.

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

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

(13) R. L. Burwell, Jr., G. L. Haller, K. C. Taylor, and J. F. Read, *Advan. Catal. Relat. Subj.*, **20**, 1 (1969).

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

(15) A. L. Dent and R. J. Kokes, *Advan. Catal. Relat. Subj.*, **22**, 1 (1972).

(16) S. Naito, H. Shimizu, E. Hagiwara, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **67**, 1519 (1971).

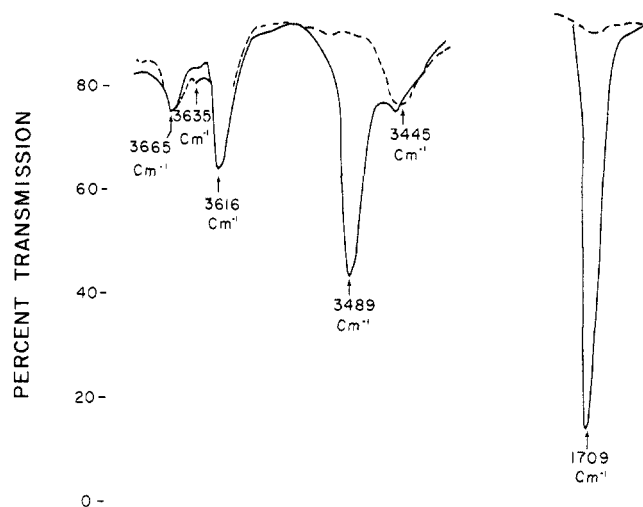
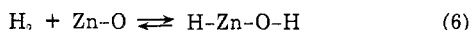
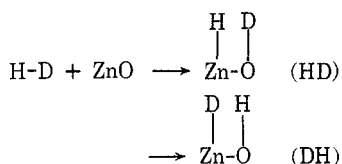


Figure 1. Spectrum of type I hydrogen on zinc oxide. The dotted line represents the background for the degassed catalyst.

Figure 1 shows the ir spectrum of hydrogen adsorbed on zinc oxide. This spectrum, characterized by strong bands at 3489 and 1709 cm^{-1} , was first reported by Eischens, Pliskin, and Low,¹⁷ who assigned these bands to stretching frequencies of an OH and ZnH surface species.¹⁸ A number of subsidiary experiments, including frequency shifts with deuterium, assure that this assignment is essentially correct. Coupled ir and adsorption experiments show that these bands stem from the type I chemisorption. Thus, it is reasonable to suppose that type I hydrogen adsorption can be represented as in eq 6, where Zn-O represents an active site.



The ir spectrum of the dissociatively adsorbed hydrogen shows that both cation and anion are involved in the active site but does not specify the relative positions of these two sites. Recent studies of isotope effects shed further light on the nature of these sites.¹⁹ At room temperature the adsorption-desorption equilibrium for type I hydrogen is rapid; at lower temperatures (below -40°C) adsorption is irreversible. Consider the adsorption of hydrogen deuteride on isolated Zn-O pair sites. Two species can form



and these can be differentiated by examination of the ir spectrum. Figure 2 shows the spectrum obtained when zinc oxide is exposed to HD at -195° . The relative intensities of the bands for DH *vs.* HD give a measure of the relative rate constants for the formation of these species; the rate of formation of

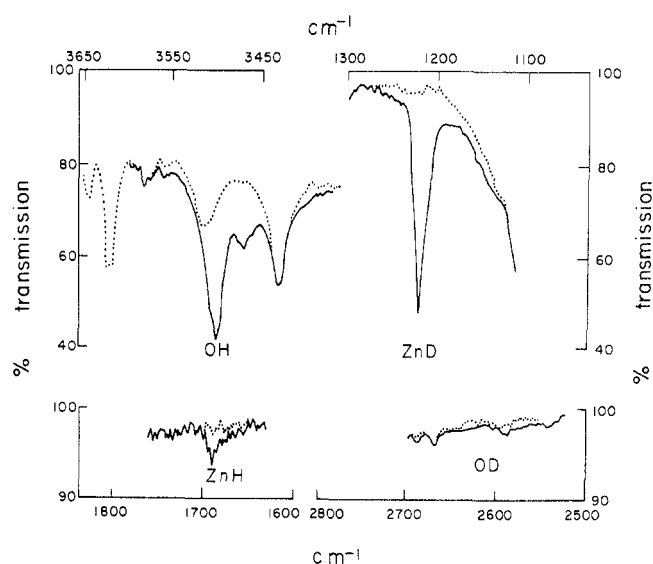


Figure 2. Spectrum of HD adsorbed on zinc oxide at -195°C . The dotted line represents the background for the degassed catalyst.

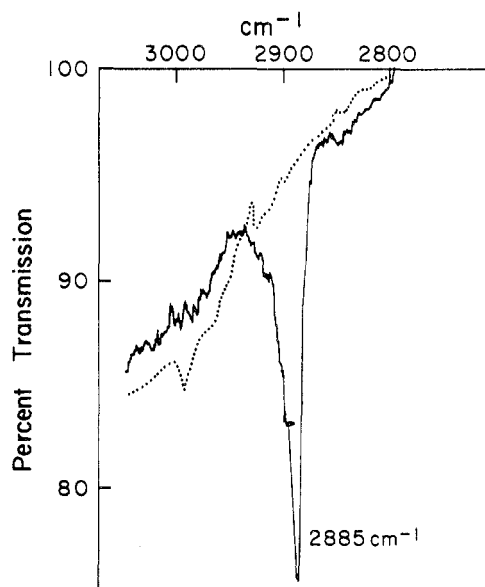


Figure 3. Spectrum of molecular deuterium on zinc oxide at -195°C . The dotted line represents the background for the degassed catalyst.

the DH is faster by nearly two orders of magnitude. By way of contrast, the thermodynamic isotope effect (at room temperature) favors HD by a factor of three. If we adsorb hydrogen deuteride at -195°C and warm the catalyst to room temperature, the preferred form changes from DH to HD; if we recool the catalyst to -195°C , the equilibrium preference for HD becomes frozen in. These results suggest that not only are the sites few in number, covering 5 to 10% of the surface, but that they consist of isolated metal-oxide pairs. Adsorption occurs directly on these sites at low temperatures and equilibrium is achieved by site-to-site migration or interchange at higher temperatures.

At low temperatures there is an additional component to the hydrogen adsorption that is not ascribable to dissociated hydrogen. This hydrogen, termed type III, represents a specific molecular form of adsorption. Figure 3 shows the band observed when

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

(18) Bending frequencies associated with these surface species have not been observed. They may be too weak to be observed or they may occur in a low frequency region (below 1150 cm^{-1}) where zinc oxide becomes so opaque that their observation is not feasible. We favor the latter interpretation.¹⁹

(19) R. J. Kokes, A. L. Dent, C. C. Chang, and L. T. Dixon, *J. Amer. Chem. Soc.*, 94, 4429 (1972).

Table I
Vibration Frequencies for Molecular Hydrogen²¹

Species	$\omega^{22}(\text{gas}),$ cm^{-1}	$\omega(\text{adsd}),$ cm^{-1}	$\Delta\omega, \text{cm}^{-1}$	$(\Delta\omega/\omega) \times 100$
H ₂	4161	4019	142	3.41
HD	3627	3507	120	3.31
D ₂	2990	2887	103	3.44

Av 3.39 ± 0.05

zinc oxide is exposed to deuterium at -195°C .²⁰ Table I lists the positions of these bands for other hydrogen isotopes²¹ along with those reported for the fundamental vibrations for the gaseous molecular species.²² There can be no doubt that the observed bands are due to molecular species with the frequencies shifted due to interaction with the surface. In the gas-phase ir, transitions due to vibrations of homonuclear diatomic molecules are forbidden, but it has been recognized for some time that such transitions can be induced by strong electric fields.²³ Thus, these bands can be ascribed to transitions made allowed by a high effective field at the surface.²⁴ Characteristics of the spectrum suggest the interaction energy is sufficient to prevent rotational motion of the molecule which occurs readily in liquid hydrogen.²¹ Nevertheless, adsorption characteristics suggest the binding is still rather weak; for example, the molecular bands disappear after brief evacuation at -195°C . Despite the low heat of binding, this molecular adsorption appears to occur on the same sites that are responsible for type I adsorption. If the catalyst is poisoned with water, the bands for both type I and molecular hydrogen no longer appear. As the catalyst is regenerated by removal of adsorbed water in stages, both bands reappear and grow in concert. These and other experiments suggest that the same active sites are utilized simultaneously for the dissociative type I and molecular adsorption. Thus, despite the fact that molecular hydrogen adsorption is weak, it appears to occur only on unpoisoned type I sites.

It seems clear that this adsorbed molecular hydrogen may play a role in reactions involving hydrogen activation. In fact, the mechanism proposed by Tamaru, *et al.*,¹⁶ for hydrogen-deuterium postulates such a molecular species. Investigations aimed at assessing its role in such reactions are now under way and suggest that the molecular species that give rise to the ir bands are the preferred intermediates in the low-temperature ortho-para conversion.²⁵ Its role (if any) in hydrogen-deuterium exchange and hydrogenation has not yet been assessed.

Intermediates in Ethylene Hydrogenation. Surface species involved in ethylene hydrogenation include adsorbed hydrogen, adsorbed ethylene, and, presumably, an adsorbed ethyl as an intermediate.

The reactive adsorbed hydrogen appears to be the type I hydrogen described in the previous section. The reactive ethylene species has an ir spectrum similar to that of a π complex;⁴ hence, in contrast to adsorbed ethylene on nickel catalysts,¹ adsorbed ethylene on zinc oxide retains its olefinic character. Furthermore, both the reacting hydrogen and ethylene are more weakly bound than on metals; in fact, they can be readily removed by brief evacuation at room temperature. In order to detect the intermediate ethyl species, we must work under dynamic conditions. Furthermore, we must be sure that any bands we see are due to an intermediate and are not produced by side reactions of the adsorbed reactants. Thus, we must search for bands with the following characteristics: (a) they must appear only under reaction conditions; (b) they must differ from bands assignable to reactants or products; (c) they must have dynamic characteristics consistent with the overall rate of reaction. Fortunately, the reaction pathway over zinc oxide is particularly well-suited for an attempt to detect this intermediate.

The surface sequence for addition of deuterium to ethylene involves no alkyl reversal; hence, we can represent it as



wherein all species but the ethane are adsorbed on the surface. By use of a short path length cell and low gas pressures, we can approach the condition that only adsorbed species contribute to the observed spectrum. If the intermediate is detectable in the ir, we should see a CD band and CH bands appear in the paraffinic region when a mixture of deuterium and ethylene is circulated over the catalyst. This is observed.²⁶ These bands are not due to adsorbed or gas-phase product ethane; if the reaction is interrupted, the catalyst is degassed, and the trapped hydrocarbons (ethane and ethylene) are reexposed to the catalyst, these paraffinic bands *do not* reappear. They *do* reappear, however, when deuterium is added again to the gas mixture. Finally, if the reaction is observed in the presence of a stoichiometric excess of deuterium, we find the paraffinic bands appear at the start of reaction, persist with little growth or decay during most of the reaction, and decay at a rate crudely comparable to that of the reaction as it nears completion. Thus, it seems reasonable to suppose that these bands are due to the intermediate.

The experiments in the circulating system had the drawback that contributions of gaseous ethylene and ethane were not completely absent; hence, although it was possible to locate some bands assignable to an intermediate, other bands may have been obscured by the spectrum of gaseous hydrocarbons. For this reason, a further series of experiments were carried out in a flow system⁴ in which the reactant stream passed through two matched path length cells in series. The first cell, in the sample beam, contained the catalyst; the second was empty. The effluent during steady-state conversion was trapped for determination of the rate. If the steady-state conversion was high enough for the ethane to contribute to the spectra, the amount

(20) C. C. Chang and R. J. Kokes, *J. Amer. Chem. Soc.*, **93**, 7107 (1971).

(21) C. C. Chang, L. T. Dixon, and R. J. Kokes, to be published.

(22) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, New York, N. Y., 1950, p 533.

(23) E. U. Condon, *Phys. Rev.*; **41** 759 (1932); M. F. Crawford and I. R. Dagg, *ibid.*, **91**, 1569 (1953).

(24) N. Sheppard and D. J. C. Yates, *Proc. Roy. Soc., Ser. A*, **238**, 69 (1957).

(25) W. C. Conner and R. J. Kokes, to be published.

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

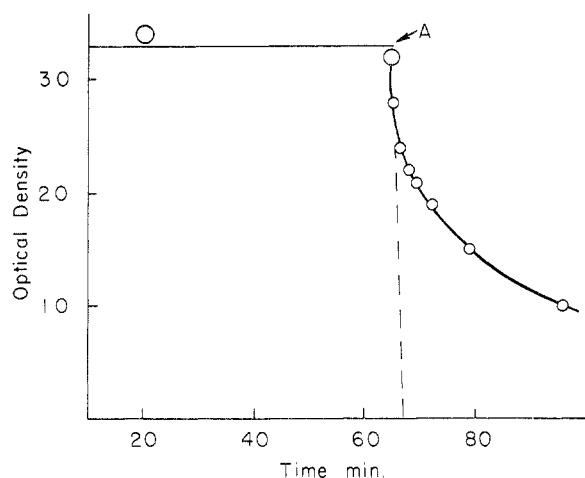
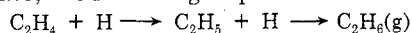


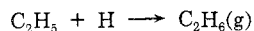
Figure 4. Intensity of the intermediate band in a flow system (see text).

of ethane in the reference beam was higher than that in the sample beam, and, hence, appeared as a negative peak. With these negative peaks as a gauge, we could increase the flow rate to the point that the contribution of the product to the spectra was negligible.

A fortunate aspect of the system made it possible to obtain reasonably good estimates of the stability of the proposed intermediate. Ethylene desorbs very rapidly. If the ethylene component of a helium-ethylene mixture is suddenly removed, the spectrum due to ethylene disappears "instantaneously" on the time scale of the experiment. Consider now the results of an experiment in which a hydrogen-ethylene mixture is passed over the catalyst until the steady state is established and, then, the ethylene is suddenly replaced by helium so that the inlet stream is a hydrogen-helium mixture. The intensity of the strongest "intermediate" band is shown in Figure 4 during the course of this experiment. We interpret this as follows. When the reacting stream is in the steady state, the following sequence occurs



The steady intensity in Figure 4 corresponds to the steady-state concentration of the intermediate. When we change to the hydrogen-helium mixture, the ethylene desorbs "instantaneously" and the decay of intensity of the intermediate represents the sequence

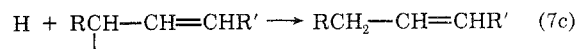


Since the initial rate of decay represents a rate-controlling step in the steady-state reaction, *this initial rate should be identical to the steady-state conversion* if the band is that of an intermediate. The estimated rate of decay is 6.7×10^{11} molecules $\text{sec}^{-1} \text{cm}^{-2}$ compared to 7.9×10^{11} molecules $\text{sec}^{-1} \text{cm}^{-2}$ for the measured steady-state rate prior to this point. The agreement of these two rates supports our assignment of this band to an intermediate.

In the simplest model, the rate of intermediate decay should be first order (or faster, if the surface hydrogen concentration builds up as the intermediate decay proceeds). In fact, the decay rate is slower than first order. We interpret this as a consequence of surface heterogeneity; in effect, this is a manifestation of the breakdown in simple rate law concepts for heterogeneous systems.

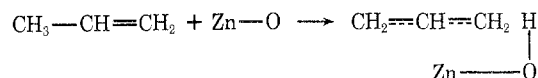
To cross-check the results with $\text{C}_2\text{H}_4\text{-H}_2$ mixtures, we also performed similar experiments with $\text{C}_2\text{H}_4\text{-D}_2$ and $\text{C}_2\text{D}_4\text{-H}_2$ reactant streams. Isotope effects make reaction rates different, but similar conclusions are reached; for example, the steady state rates and estimated decay rates with $\text{C}_2\text{H}_4\text{-D}_2$ are 3.3×10^{11} and 4.5×10^{11} molecules $\text{sec}^{-1} \text{cm}^{-2}$, respectively. These rates are the same within the admittedly large experimental error. Details of the assignment of the intermediate bands are beyond the scope of this presentation. It should be noted, however, that the various deuterated intermediates examined ($^*\text{-CH}_2\text{CH}_3$, $^*\text{CH}_2\text{CH}_2\text{D}$, $^*\text{CD}_2\text{CD}_2\text{H}$) provide cross-checks of the assignment. In sum, our analysis leads to the conclusion that the intermediate is an ethyl radical bound to the zinc half of the zinc-oxygen pair site.⁴

Intermediates in Olefin Isomerization. Burwell and coworkers¹³ have suggested that formation of an allylic species followed by a 1,3 hydrogen shift may provide a pathway for olefin isomerization over chromia, *viz.*



Such an allylic intermediate may play a broad role in catalytic reactions over oxides. In recent years mechanistic evidence has accumulated that allylic species are also intermediates in oxidation of olefins.²⁷ It has been pointed out that the formation of such a species by dissociative adsorption is especially favored by the inherent lability of the allylic hydrogen.

If, indeed, the above mechanism prevails, one would expect ethylene and propylene adsorption on zinc oxide to be dramatically different. Ethylene does adsorb to form a π complex which is readily removed by evacuation at room temperatures.⁴ Propylene also adsorbs to form a π complex with similar characteristics, but it also forms another species which is removable (as such) only by evacuation at 125°C for about 1 hr.⁵ Infrared studies show that this strongly held species is dissociative inasmuch as a new OH band appears when this species forms. Studies with six different deuterium labeled-propylenes show that the hydrogen responsible for the OH band comes from the methyl hydrogen. Analysis of the data suggests that adsorption of this species can be represented as



wherein $\text{CH}_2=\text{CH}=\text{CH}_2$ represents a symmetric, π -bonded allylic species in which the CCC angle is close to 120° and the CC bonds have half double bond character.⁵ We term this species the π -allyl.

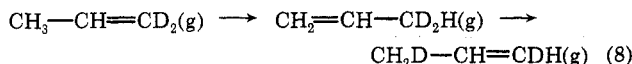
We can study the 1,3 hydrogen shift by examination of what happens to $\text{CH}_3\text{CH}=\text{CD}_2$ when it is exposed to zinc oxide. If 1,3 transfer occurs, we would expect the reaction in eq 8. Thus, in the early stages of

(27) H. H. Voge and C. R. Adams, *Advan. Catal. Relat. Subj.*, 17, 154 (1967).

Table II
Products from $\text{CH}_3\text{CH}=\text{CD}_2$ Isomerization

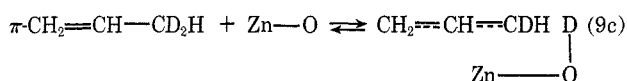
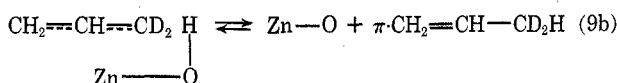
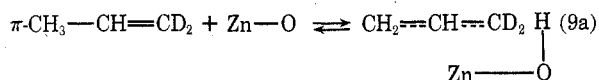
Compound	%	% at equilibrium ^a
$\text{CD}_2=\text{CHCH}_3-x\text{D}_x$	30 ± 2	10
$\text{CH}_2=\text{CHCH}_3-x\text{D}_x$	59 ± 3	30
$\text{CHD}=\text{CHCH}_3-x\text{D}_x$	10 ± 4	60

^a This was calculated assuming a random distribution of deuterium on the end carbons with no isotope effect.



reaction, $\text{CH}_2=\text{CHCD}_2\text{H}$ should be the dominant product. When equilibrium is achieved, however, assuming a random distribution, the concentration of $\text{CH}_2\text{DCH}=\text{CDH}$ should be twice that of $\text{CH}_2=\text{CHCHD}_2$. Table II lists the products observed (as analyzed by ir) when $\text{CH}_3\text{CH}=\text{CD}_2$ is circulated over zinc oxide for several hours. We are still far from equilibrium and the dominant species is, as expected, $\text{CH}_2=\text{CHCD}_2\text{H}$. In line with the proposed scheme (eq 8), the ir spectrum of the products suggests that no deuterium appears on the central carbon atom. Presumably, the sites capable of π -allyl formation are saturated; hence, we would expect the rate to be zero order. Because this represents a *limiting* rate law, we would expect this behavior to be approached even if the surface is heterogeneous. On this basis the rate of catalytic conversion is 3.7×10^{10} molecules $\text{sec}^{-1} \text{cm}^{-2}$.

We can also study this reaction by infrared techniques. Consider what happens when $\text{CH}_3\text{CH}=\text{CD}_2$ is adsorbed on the surface under conditions such that all of it is adsorbed. We expect the following surface reactions to occur:



etc.

We can follow these changes by observing the OH and OD region of the spectrum as a function of time. If we wait long enough, we would expect the ratio of surface OH to OD to change from an initial ratio of 1.0:0 to an equilibrium ratio of 0.6:0.4 since, in time, the two ends of the molecule become equivalent. Figure 5 shows a plot of the estimated amounts OH and OD *vs.* time. It seems clear that the time dependence corresponds at least roughly to that expected. The half-time for the OH decay of $\text{CH}_3\text{CH}=\text{CD}_2$ is about 40 min if we assume the intensity after 7 hr represents equilibrium. For first-order behavior, this yields a rate of 2.9×10^{10} molecules $\text{sec}^{-1} \text{cm}^{-2}$. This represents the rate of reactions 9a through 9c. If we assume reaction 9c is rapid compared to 9b (or desorption), the rate of OH disappearance *via* reaction 9b will be two-thirds the rate of the *surface* isomerization of $\text{CH}_3\text{CH}=\text{CD}_2$.

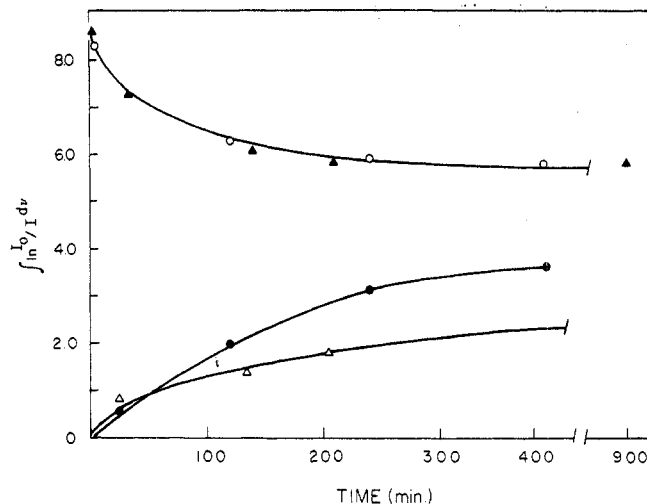
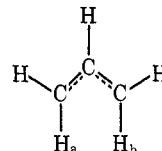


Figure 5. Integrated intensity of OH and OD bands *vs.* time for adsorbed labeled propylenes: O, OH, ●, OD for $\text{CH}_3\text{CH}=\text{CD}_2$; Δ, OH, ▲, OD for $\text{CD}_3\text{CH}=\text{CH}_2$.

Thus, if the surface rate is rate controlling, we would expect the catalytic experiment to yield a rate of 4.3×10^{10} molecules $\text{sec}^{-1} \text{cm}^{-2}$. In view of the pyramidding of approximations in this estimate, this is in excellent agreement with the observed catalytic rate 3.7×10^{10} molecules $\text{sec}^{-1} \text{cm}^{-2}$. This agreement strongly suggests that the species observed in the ir, the π -allyl, is the species responsible for the 1,3 hydrogen shift, *i.e.*, the "isomerization" of propylene.

In view of the results with propylene, it seems reasonable to expect that isomerization of butenes will also proceed *via* π -allyl species. There are, however, a number of added features we might expect. Propylene forms two species on adsorption.⁵ One of these, designated as a π complex, is readily removed by brief evacuation at room temperature; this species results from nondissociative adsorption and, like its ethylene counterpart,⁴ is characterized in the ir, in part, by a double bond frequency about 30 cm^{-1} below that for gaseous propylenes. The π -allyl, on the other hand, is a dissociatively adsorbed species removable only by evacuation at elevated temperature; it is characterized, in part, by a double bond frequency about 107 cm^{-1} below that for gaseous propylene. The presumed structure is planar and symmetric as indicated below with the plane of the



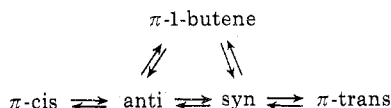
molecule parallel to the surface above a zinc atom.⁵ With butenes we expect five adsorbed species. Three of these would be π complexes of *cis*-, *trans*-, and 1-butene. The remaining two would be a *syn* or an *anti* π -allyl complex, so termed because hydrogens or a hydrogen and a methyl (respectively) can occupy the a,b positions indicated above. *Cis* and *trans* π complexes should form *anti* and *syn* π -allyls, and 1-butene π complexes could form either π -allyl.

Analysis of the results for butene isomerization is intricate;^{28,29} hence, we shall only summarize the

(28) C. C. Chang, W. C. Conner, and R. J. Kokes, to be published.

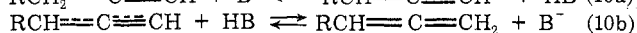
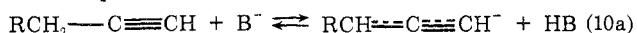
(29) R. J. Kokes, *Intra-Sci. Chem. Reports* 6, 77 (1972).

results here. Dynamic ir studies reveal bands assignable to all five species and suggest that isomerization occurs *via* the following surface sequence:



The bands in the double bond region for these species, moreover, occur at positions predictable on the basis of observations for adsorbed propylene. Kinetic studies show that, once again, the surface reaction is rate controlling. Mechanistic implications of the relative rate constants suggest that the allyl species bound to the surface zinc has considerable anionic character; hence, catalysis by zinc oxide resembles, to some degree, homogeneous base catalysis.

Isomerization of Acetylenes. The reaction pathway for the base-catalyzed acetylene-allene isomerization is presumed to be³⁰



The similarity of this pathway to the corresponding one for olefins is striking. Both involve 1,3 hydrogen shifts; both involve carbanions stabilized by resonance. Infrared studies reveal that such a parallelism is also found for adsorption and reaction of zinc oxide.³¹ The salient features of the adsorption experiments are: (1) methylacetylene adsorbs to give an OH band and a hydrocarbon species characterized, in part, by a band at 1865 cm⁻¹; (2) 1-deuteriomethylacetylene adsorbs to give initially an OH band rather than an OD band; (3) the spectrum of adsorbed allene is essentially identical with that of methylacetylene. These observations are clearly consistent with the formation of the propargyl species, CH₂=C≡CH, as depicted in eq 10 (R = H). The first result shows that a hydrogen is removed from the methylacetylene, thereby yielding a band at 1865 cm⁻¹, which is too high to be a simple double bond but is much lower in frequency than that for the triple bond in gaseous methylacetylene (2142 cm⁻¹). The second result shows that the hydrogen is removed from the methyl group. The third result suggests formation of the propargyl species by reversal of reaction 10b. Thus, it is expected that zinc oxide would be a catalyst for this reaction. Rate studies show that it is, indeed, a catalyst; the rate is roughly zero order with a catalytic rate of about 5 × 10¹⁰ molecules sec⁻¹ cm⁻².

Dynamic ir studies of the spectrum of adsorbed CH₃C≡CD provide data on the rate of the surface reaction. We consider that the band at 1865 cm⁻¹ corresponds to the C=C≡CH group. If we assume that the hydrogen bound to this carbon moves with it and that the C=C bond is so soft that it is decoupled from this vibration, the effective reduced mass becomes 6.24 amu. Then, when deuterium is bound to the end carbon, the reduced mass would be 6.46 amu and the frequency should shift by a factor of

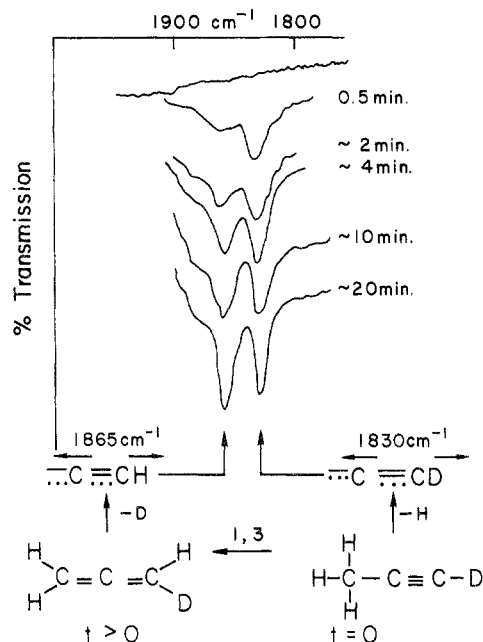
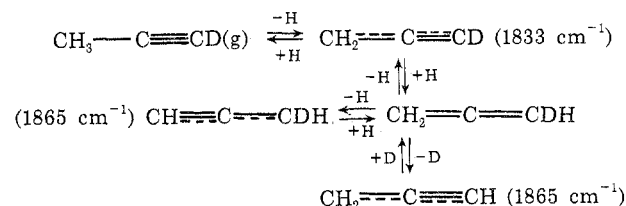


Figure 6. Spectrum of CH₃C≡CD on zinc oxide. Numbers refer to times after admission. The dotted line represents the background for the degassed catalyst.

(6.24/6.46)^{1/2}, *i.e.*, to 1833 cm⁻¹. Now consider the expected surface sequence after adsorption of a small dose of CH₃C≡CD.



Repeated scans in the 1800–1900-cm⁻¹ region should reveal initial formation of a band at about 1833 cm⁻¹; in time, a band should appear at 1865 cm⁻¹ and, ultimately, the later formed band should have the greater intensity. Figure 6 shows this behavior is observed. With some assumptions, we can estimate the rate of the surface 1,3 hydrogen transfer from these data. The estimated surface rate is of the order of 10¹² molecules sec⁻¹ cm⁻². Since the surface rate is much faster than the catalytic rate, we can conclude that the slow step is probably desorption of the nearby equilibrated surface species rather than the surface reaction itself.

Summary. Determination of intermediates and characterization of their structure and their dynamic behavior is a worthy ambition, but the feasibility of this objective depends strongly on the system chosen for investigation. In large part, the successes achieved for zinc oxide stem from the fact that it is a particular kind of poor catalyst. A catalyst can be poor either because the intermediates do not form readily or because they are hard to decompose. Zinc oxide appears to be a poor catalyst because the intermediates decompose with difficulty. This means that under reaction conditions their concentration can become high enough to observe in the infrared. Not all systems can be expected to behave in this

(30) I. Iwai in "Mechanism of Molecular Vibrations," Vol. 2, B. S. Thyarajan, Ed., Wiley, New York, N. Y. 1969, p 13.

(31) C. C. Chang and R. J. Kokes, *J. Amer. Chem. Soc.*, **92**, 7517 (1970); *J. Catal.*, **28**, 92 (1973).

manner. We believe, however, that every class of catalysts, metals, acidic oxides, etc., probably has a member of the class that approaches being a poor catalyst in the right way for infrared detection of intermediates to be feasible. For these, infrared studies under dynamic conditions approximating those used in conventional catalytic studies can be coupled with

tracer techniques and traditional studies to yield a detailed picture of the reaction sequence.

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Effects of Molecular Reorientation on Electron Spin Resonance Spectra

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It has now become commonplace for chemists to observe and measure a variety of processes—conformational changes, rotational and translational diffusion, chemical reactions—by their effects on magnetic resonance spectra. In many instances increasing rates are accompanied by narrowing of spectral responses. To a senescent spectroscopist nurtured on the doctrine that enhancement of spectral resolution in dense media was to be sought by freezing out troublesome molecular motions through use of low temperatures and high viscosities, there is a sense of delight not only because the doctrine is wrong but because examination of its failures has shown how analysis of spectra can often reveal features of the motions not previously experimentally accessible.

Some of the ruminations in the succeeding pages may appear to be naive; they represent my attempts to get an intuitive grasp of the phenomena. "Intuitive grasp" here means the ability to obtain qualitative relations without lengthy formal calculations. In this article I discuss only a few applications of the ideas to some of the effects of rotational diffusion on magnetic resonance spectra, in particular the way in which the dipole-dipole interaction responds to such rotational motion. The reader who seeks mathematically satisfying rigorous treatments of the phenomena is referred to the recent work listed in the first reference¹ and to the earlier works cited in them.

We start with a description of the dipole-dipole interaction and its application to a familiar case—the proton magnetic resonance spectra of water. Although the calculations are usually carried out through use of the Hamiltonian form of the interac-

tion, we use the dipolar field because of its readier conceptualization.

Consider a dipole μ situated at the center of a sphere. The field at each point on the sphere depends in direction and magnitude on the orientation of its radius vector relative to the dipole. At each orientation the magnitude of the field is inversely proportional to the cube of the radius. The angular dependence may be represented by the variation on the spherical surface. The field at each orientation lies in the plane defined by the direction of the dipole and the radius vector. Its component parallel to the dipole at a point whose radius vector makes angle θ with the dipole is proportional to $\frac{1}{3} + \cos 2\theta = \frac{2}{3}(3\cos^2 \theta - 1)$; the component perpendicular to the dipole varies as $\sin 2\theta = 2 \sin \theta \cos \theta$. The energy of interaction, E_{12} , between two dipoles is the negative of the scalar product of the field at one of the dipoles with its dipole moment; *i.e.*, $-E = \mathbf{H}_1(r_2) \cdot \mu_2 = \mathbf{H}_2(r_1) \cdot \mu_1$, where $\mathbf{H}_1(r_2)$ is the field at position of dipole μ_2 produced by dipole μ_1 and $\mathbf{H}_2(r_1)$ is the field at dipole μ_1 produced by μ_2 . The familiar Hamiltonian form of the interaction exhibits its symmetry

$$H_{12} = \frac{1}{r^3} \left[\mu_1 \cdot \mu_2 - \frac{3(\mu_1 \cdot \mathbf{r})(\mu_2 \cdot \mathbf{r})}{r^2} \right]$$

where r is the distance between dipoles and \mathbf{r} the vector joining them. The interaction may be expanded in products of components of the two dipole vectors; the coefficients form a tensor of zero trace.

The dipolar interaction described above is sufficient to account for the effects of rotation in many instances in which identical spins in equivalent environment interact. Examples are the proton resonance in water and the electron spin resonance in a

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(1) M. Fixman, *J. Chem. Phys.*, **48**, 534 (1968); H. Sillescu and D. Kivelson, *ibid.*, **48**, 3493 (1968); R. G. Gordon, *Advan. Magn. Resonance*, **3**, 1 (1969); H. Silliscu, *J. Chem. Phys.*, **54**, 2110 (1971); J. H. Freed, G. V. Bruno, and C. Polnaszek, *ibid.*, **55**, 5270 (1971); R. M. Lynden-Bell, *Mol. Phys.*, **22**, 837 (1971).