metric carbon–carbon stretch is probably a multiple band. In most cases this band is merely broad, but for perdeuteriopropylene (Figure 5) the structure of the band is evident. This structure can be rationalized if we assume that similar but slightly different sites are involved in the chemisorption. The differences in bonding to these different sites would be more likely to manifest themselves in the carbon–carbon bond, involved in π bonding, than for the once-removed carbon–hydrogen bond. In this event, structure in the vibrational bands for the allyl species could be evident for the carbon–carbon frequencies but not for the carbon–hydrogen frequencies. This means that if we include only the most prominent carbon–carbon band (the maximum) in our analysis, we are justified in treating the spectrum as if it were that for a single species.

Finally, we should note that although the treatment of the adsorbed allyl as a vibrationally independent system is an approximation, it does make it possible to utilize procedures commonly used in discussions of the spectrum of liquids and gases. Results of this treatment provide stronger support for and a more detailed picture of the structure of the adsorbed species than a more primitive interpretation of the spectrum. Accordingly, we feel the approximation is a valuable one which may be applied cautiously with profit to infrared studies of adsorbed species.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The authors also acknowledge the benefit of many helpful discussions of this work with Professor D. W. Robinson.

The Nature of Adsorbed Propylene on Zinc Oxide. II. Reactions of π-Allyl Species

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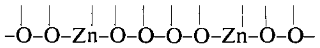
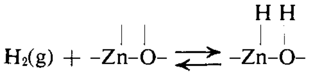
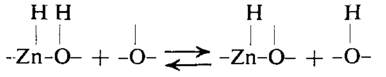
Abstract: The reaction over zinc oxide of propylenes (labeled and unlabeled) in the presence and absence of deuterium has been studied both by traditional mechanistic and infrared techniques. Isomerization of labeled propylene (intramolecular hydrogen exchange) and intermolecular hydrogen exchange occur at roughly comparable rates. Furthermore, propylene–deuterium exchange occurs at a rate competitive with the addition reaction and the product contains a distribution of deuteriopropanes. Comparison of these results with those obtained for ethylene leads to the conclusion that those reactions that occur only with propylene are a consequence of the formation of reactive π-allyl species.

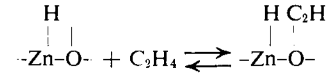
Hydrogenation of ethylene over zinc oxide has been the subject of several recent papers from this laboratory.[1-4] These studies led to the conclusion that hydrogen adsorption and reaction occur on isolated, independent, active sites consisting of adjacent zinc and oxygen ions. It was suggested that these sites arise from surface reconstruction in which zinc ions systematically fill the trigonal holes in a surface layer of oxide ions defining a close-packed array. Schematically, we can picture this surface as follows

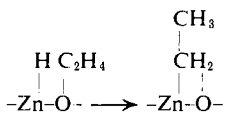

$$\text{-O-O-Zn-O-O-O-O-Zn-O-O-}$$

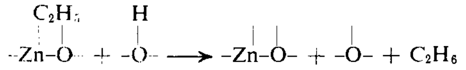
wherein the neighboring zinc and oxygen atoms represent active sites. The *principal* steps in the suggested mechanism are


$$\mathrm{H_2(g)} + \text{-Zn-O-} \rightleftharpoons \overset{\mathrm{H\ H}}{\text{-Zn-O-}} \qquad (1)$$


$$\overset{\mathrm{H\ H}}{\text{-Zn-O-}} + \text{-O-} \rightleftharpoons \overset{\mathrm{H}}{\text{-Zn}}\text{-O-} + \overset{\mathrm{H}}{\text{-O-}} \qquad (2)$$


$$\overset{\mathrm{H}}{\text{-Zn}}\text{-O-} + \mathrm{C_2H_4} \rightleftharpoons \overset{\mathrm{H\ C_2H_4}}{\text{-Zn-O-}} \qquad (3)$$


$$\overset{\mathrm{H\ C_2H_4}}{\text{-Zn-O-}} \longrightarrow \overset{\overset{\mathrm{CH_3}}{|}}{\overset{\mathrm{CH_2}}{\text{-Zn-O-}}} \qquad (4)$$


$$\overset{\mathrm{C_2H_5}}{\text{-Zn-O-}} + \overset{\mathrm{H}}{\text{-O-}} \longrightarrow \text{-Zn-O-} + \text{-O-} + \mathrm{C_2H_6} \qquad (5)$$

where —Zn—O— represents the active site and -O- a surface oxygen atom between sites. The basis for this scheme has been discussed elsewhere.[3] Salient features pertinent to the current work are: (a) infrared studies are consistent with this scheme insofar as they suggest that ethylene chemisorbs (weakly) without dissociation and with the double bond intact to form a weak "π complex";[5] (b) because of the nature of adsorbed ethylene and the irreversibility of steps 4 and 5, addition of deuterium to ethylene leads cleanly to $C_2H_4D_2$;[1] (c) step 2 in the above scheme, which provides for site-to-site hydrogen migration, is required to explain the observed H_2–D_2 exchange.[2]

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* Address correspondence to this author.

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

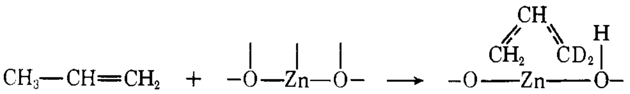
[2] W. C. Conner and R. J. Kokes, *J. Phys. Chem.*, 73, 2436 (1969).

[3] A. L. Dent and R. J. Kokes, *ibid.*, 73, 3772, 3781 (1969).

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

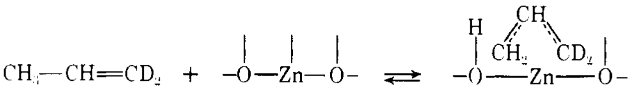
[5] A. L. Dent and R. J. Kokes, unpublished results.

In the preceding paper, we presented evidence that propylene adsorbed on zinc oxide forms a π-allyl species.[6,7] The data suggest that adsorption occurs on sites similar to those depicted in the foregoing scheme, *viz.*

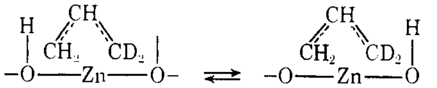


(6)

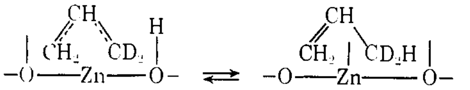
(for reasons that will become apparent shortly, we need a more detailed representation of the active site than in steps 1-5.) Such a mode of adsorption provides a mechanism for double-bond isomerization in the absence of hydrogen. We can follow such isomerization by use of labeled propylenes. For example, on the basis of the foregoing, we expect the following sequence for adsorbed $CH_3—CH═CD_2$



(7)



(8)



(9)

Step 8 in the above is the analog of step 2, which is required for H_2-D_2 equilibration; it is a necessary step if we view the π allyl as an immobile species on the surface. The products of step 9 can be viewed as propylene in the form of a loosely held π complex[7] which on desorption yields isomerized propylene. Readsorption of the isomerized propylene (or further reaction of the π complex) would be expected to yield surface OD groups. In addition to isomerization of propylene (by intramolecular hydrogen migration) steps 7-9 provide a means for intermolecular hydrogen migration; hence, in the presence of zinc oxide the labeled propylene $C_3H_4D_2$ should lead, in time, to a variety of products of the form $C_3H_{1+x}D_{5-x}$ with an average deuterium content of two per molecule and no exchange of the hydrogen bound to the central carbon atom. Finally, if the π allyl plays a role in hydrogenation reactions, we would expect that addition of deuterium would result in exchange of propylene with deuterium *via* the analog of steps 1 and 2 and 7-9 and that the resultant propane would be of the form $C_3H_{8-x}D_x$.

Thus, if the π allyl formed from adsorbed propylene is a reactive species, we would expect the following reactions to occur. (1) $CH_3—CH═CD_2$ should isomerize over zinc oxide in the absence of hydrogen by intramolecular hydrogen transfer to form initially $CH_2═CH—CD_2H$ and, in time, $CHD═CH—CH_2D$. (2) Intermolecular hydrogen transfer should occur in the foregoing reaction or in related systems (*e.g.*, a mixture of C_3H_6 and C_3D_6). (3) Exchange of deuterium with propylene should occur during the addition of deuterium to propylene. (4) Propane formed by addition of deuterium to propylene should lead to a distribution of products of the form $C_3H_{8-x}D_x$ with $0 \leq x \leq 8$. This work was carried out to test these predictions.

Experimental Section

Materials, pretreatment, and procedures for infrared studies of chemisorbed propylene as a function of time were essentially the same as those described in the preceding paper.[7]

Kinetic studies were carried out in a closed system with forced circulation by a magnetically driven piston. The circulation rate was 500 cm³/min at atmospheric pressure. The reaction loop, including the catalyst tube, had a volume of about 125 cm³; it was provided with in-line traps and provisions for sampling for chromatographic or mass spectrographic analysis. For studies of isomerization, C_3H_6-C_3D_6 exchange, and C_2H_4-C_2D_4 exchange, a 10-g sample (ZnO-24:Kadox) was the catalyst. For studies of hydrogenation a 5.0-g sample (ZnO-21:Kadox) was used. Both catalyst samples were pressed into disks as for ir studies and then broken into large pieces; this procedure not only provided a partial match of the catalyst history to that of samples used for infrared studies, it also improved the flow characteristics. Activation procedures were the same as those used in ir studies.

In isomerization studies about 300 mm of $CH_3—CH═CD_2$ was circulated over the catalyst. At the conclusion of the experiment the products were divided into two portions. The first portion, designated as gaseous product, was the product collected by condensation for 15 min in a liquid nitrogen trap. The second portion, designated as surface product, was the 3.7 cm³ of chemisorbed propylene collected by degassing the catalyst for 1 hr at 125°.

Analysis of the products of the reaction of $CH_3—CH═CD_2$ over zinc oxide was based on the ir spectrum of the gaseous products in the 700–925-cm⁻¹ region where the spectrum of pure deuteriopropylenes has several strong, sharp, characteristic Q branches. These band positions plus the absorbances are listed in Table I for several pure compounds. The sharp band in compounds II and IV at 910–915 cm⁻¹ is due to the $>C═CH_2$ out-of-plane bend (ν_{19}).[8] The sharp band at 725 cm⁻¹ in compounds I and III is due to the corresponding $>C═CD_2$ vibration.[8] One would expect the analogous vibration for $>C═C(—H)—D$ to occur at 800–825 cm⁻¹. For analytical procedures it is particularly important to note that the band positions and absorbances for these bends are insensitive to the isotopic composition of the methyl group (compare I and III). This provides the basis for analysis. (Bands due to the out-of-plane bend of the central C-H occur between 950 and 1000 cm⁻¹, depending on the isotope. The band at 850 cm⁻¹ for compound IV is assigned to the corresponding C-D vibration.)

Table I. Spectrum of Pure Labeled Propylene[a]

	Compound	Band positions, cm⁻¹	Log (I_0/I)
I	$CH_3—CH═CD_2$	725	0.568
		910	0.252
II	$CD_3—CH═CH_2$	910	0.575
III	$CD_3—CH═CD_2$	725	0.600
IV	$CH_3—CD═CH_2$[b]	915	0.700
		850	0.225

[a] These bands are the sharp Q bands between 700 and 925 cm⁻¹ for samples at 20 mm of pressure in a 10-cm path-length cell and with 1.0-cm⁻¹ spectral slit widths. [b] This sample was run at a pressure greater than 20 mm; a relatively weak doublet at 825 cm⁻¹ was unassigned.

Figure 1 shows a typical spectrum at 20 mm of the products of reaction of $CH_3—CH═CD_2$ over zinc oxide. Composition was computed by two procedures. In the first procedure data in Table I for compounds I and II were used to compute the absolute amounts of $>C═CH_2$ and $>C═CD_2$, and the amount of $>C═CHD$ was determined by difference. In the second procedure peaks near 800 cm⁻¹ were assumed to be due to a $>C═C(—H)—D$ bend, and, with the assumption that the absorbance was the mean of that for

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

(7) A. L. Dent and R. J. Kokes, *ibid.*, **92**, 6709 (1970).

(8) R. C. Lord and P. Venkataswarlu, *J. Opt. Soc. Amer.*, 43, 1079 (1953).

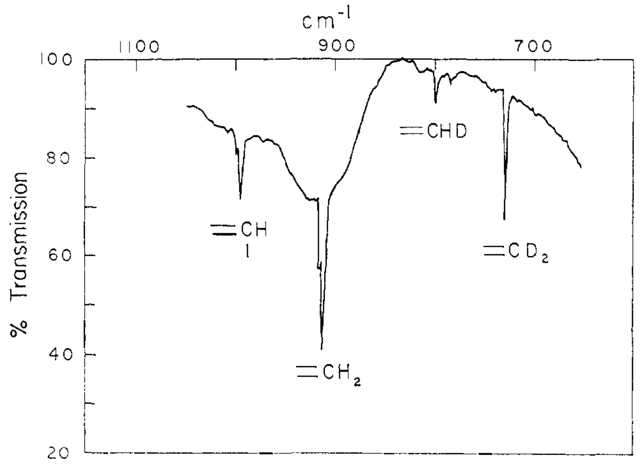

Figure 1. Spectrum of isomerized CH_3—CH=CD_2, pressure = 20 mm, spectral slit width = 1.0 cm^{-1}.

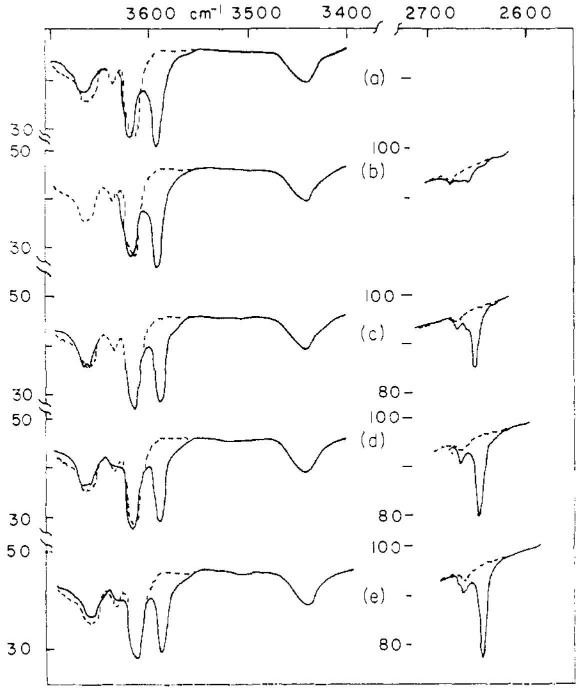

Figure 2. Spectrum of adsorbed CH_3—CH=CD_2 as a function of time in the OH and OD region (the left side is the OH region; the right side is the OD region): (a) after ~5 min, (b) after ~30 min, (c) after ~120 min, (d) after ~240 min, (e) after ~390 min.

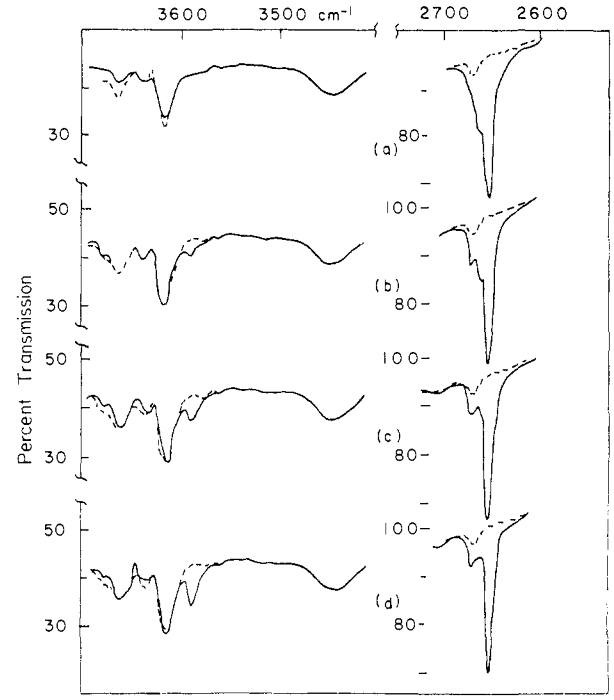

Figure 3. Spectrum of adsorbed CD_3—CH=CH_2 as a function o time in the OH and OD region (the left side is the OH region; the right side is the OD region): (a) after ~1 min, (b) after ~30 min, (c) after ~80 min, (d) after ~900 min.

the other species, the composition was computed. Both procedures yielded similar results. The listed uncertainty in the reported data represents the disagreement in the two procedures.

Deuterium assay of the products of reaction was obtained by mass spectrographic analysis. For olefins the ionizing voltage was adjusted so that only parent peaks were observed. For paraffins low voltages were also used but fragmentation occurred; hence, a small correction, based on the usual statistical assumptions, was made.[9]

Results and Discussion

The Absorbed Species. Figure 2 shows the change with time in the OH and OD region of the spectrum of chemisorbed CH_3—CH=CD_2.[10] In these runs the catalyst was first exposed to propylene at 20 mm; then, the gas-phase and weakly adsorbed propylene was removed by condensation in a liquid nitrogen trap. Thus, the amount of π complex[7] and gas-phase propylene was essentially zero. Immediately after adsorption, an OH band appears at 3593 cm^{-1}; in time the OH band decreases in intensity and an OD band appears at 2653 cm^{-1} and grows in intensity. This OD band cannot be due to exchange; the growth of the OD band is not accompanied by any decrease in the surface hydroxyl bands. The amount of exchange that does occur is limited to an amount corresponding roughly to the very small peak seen in the background.

As the OD band grows in intensity changes are evident in the hydrocarbon portion of the spectrum. These changes are too complex for detailed interpretation, but the multiplicity and the nature of the bands that develop clearly suggest that more than one hydrocarbon species is present on the surface.

Changes in the OH and OD region of the spectrum of chemisorbed CD_3—CH=CH_2 as a function of time (Figure 3) reveal a pattern paralleling that in Figure 2. Now, of course, the roles of the OH and OD species are interchanged.

The integrated absorbances of the OH and OD bands for chemisorbed CH_3—CH=CD_2 and chemisorbed CD_3—CH=CH_2 are plotted *vs.* time in Figure 4. One would expect the absorption coefficients of OH and OD to differ,[11] and studies with adsorbed hydrogen and deuterium[5] suggest that the absorption coefficient of OH is greater than that for OD by a factor approximately equal to the square of the isotopic

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(9) The corrections at low voltage were based on cracking patterns of standard compounds (*e.g.*, ethane-d_0, ethane-d_2–1,2-propane-d_0, and propane-d_6). Statistical distributions were calculated on this basis for the deuterioethane and deuteriopropane series.

(10) We shall reserve the term OH for species formed by absorption. Bands due to surface hydroxyl groups appearing in the zinc oxide background spectrum will be referred to as hydroxyl bands. A similar convention will be used for the corresponding deuterium species.

(11) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 192.

Table II. Product Analysis of Isomerized $CH_3—CH=CD_2$

Compound	Gaseous[a] product obsd, %	Gaseous[b] product equilibrium, %	Surface[a] product obsd, %	Surface[b] product equilibrium, %
	Infrared Analysis			
A $CD_2=CH—CH_{3-x}D_x$	30 ± 2	11	8 ± 1	12
B $CH_2=CH—CH_{3-x}D_x$	59 ± 3	31	64 ± 2	40
C $CHD=CH—CH_{3-x}D_x$	10 ± 4	58	28 ± 2	48
	Mass Spectroscopic Analysis			
C_3H_6	0.6	8	8.9	10.8
C_3H_5D	9.9	26	27.5	30.2
$C_3H_4D_2$	79.0	35	41.6	34.0
$C_3H_3D_3$	10.0	23	17.8	19.0
$C_3H_2D_4$	0.6	8	4.1	5.4
Av D/molecule	1.99		1.80	

[a] See the Experimental Section for definitions. The products were collected after 6 hr of reaction at room temperature. The total pressure was 300 mm. [b] These values were computed from the experimentally determined deuterium content with the assumption that the distribution of deuterium between the end carbons was random.

shift, 1.81, as predicted from theory. However, the OH and OD formed by adsorption of C_3H_6 and C_3D_6 (or C_3H_5D and C_3HD_5), respectively, yield absorption coefficients whose ratio is approximately equal to the isotopic shift, 1.35. We cannot resolve this discrepancy without invoking a possible combination of unusual anharmonicity and hydrogen-bonding effects on the OH stretching frequency. Accordingly, even though theory suggests a larger factor for the absorption coefficient ratio, we have in Figure 4 multiplied the integrated absorbance of OD by 1.35. Thus, the values given should be proportional to the number of OD and OH species on the surface. The agreement suggests this procedure is basically correct.

The changes in integrated intensity with time (Figure 4) are consistent with the scheme depicted in eq 7–9. According to this scheme $CH_3—CH=CD_2$ should yield only surface OH initially. Reiteration of these reactions with the product $CH_2=CH—CD_2H$, however, should lead to the appearance of an OD species on the surface. In time an equilibrium should be reached with OH and OD species in a ratio of 3 to 2 provided there is no isotope effect. (The same results with the role of OH and OD species reversed is expected for $CD_3—CH=CH_2$.) The arrows in Figure 4 indicate the expected asymptotic values for the upper and lower curves. Except for the OH species[12] from $CD_3—CH=CH_2$, these values are closely approached.

Propylene Isomerization. Table II summarizes the results of a $CH_3—CH=CD_2$ isomerization run. The first three products listed (A, B, and C) were determined, as described in the Experimental Section, by ir analysis; the number of deuteriums per molecule was determined by mass spectrographic analysis. The products showed no evidence of a band at 850 cm^{-1} assignable to an out-of-plane bending of a deuterium attached to the central carbon atom; hence, it appears that the inter- and intramolecular hydrogen exchange involves primarily the end carbon atoms.

Consider the first three components listed for the gaseous products and ignore for the moment the fact that some intermolecular hydrogen transfer accompanies the isomerization reaction. Random statistics favor C as a product; despite this, B is the major initial product. This suggests that to a first approximation equilibrium is achieved by the following pathway

$$A \rightleftarrows B \rightleftarrows C$$

This is the pathway one would expect by the scheme depicted in eq 7–9; on this basis, $CH_2=CH—CD_2H$, corresponding to B, should be the initial product.

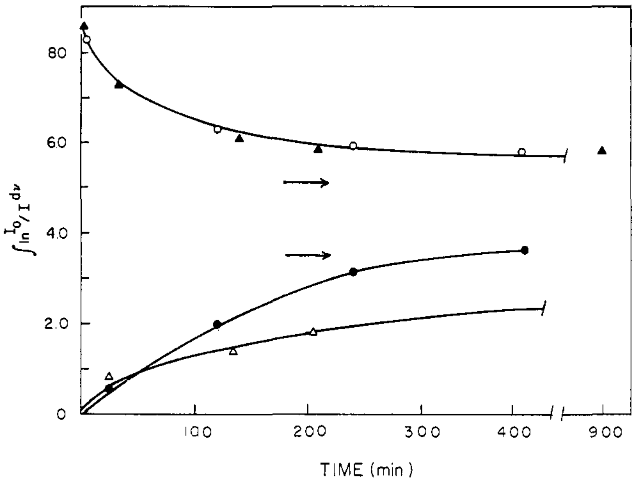

Figure 4. Integrated intensity of OH and OD bands *vs.* time for adsorbed labeled propylenes: ○, OH; ●, OD for $CH_3—CH=CD_2$; △, OH; ▲, OD for $CD_3—CH=CH_2$. The integrated intensity for OD was multiplied by 1.35, the isotopic shift, in an attempt to correct for expected differences in integrated absorption coefficient.

The presence of intermolecular deuterium exchange does in fact complicate the analysis of the data. Nevertheless, for the gaseous products with exchange the computed equilibrium A:B:C = 11:31:58 is only slightly different from that expected in the absence of exchange, A:B:C = 10:30:60. Accordingly, it seems reasonable to suppose that the effect of exchange is a minor perturbation and the foregoing interpretation is still the correct one.

It is of some interest to compare the rates in these experiments to those obtained in Figure 4. The experimental conditions were such that the propylene in the gas phase was about 42 cm^3 STP, whereas the amount of chemisorbed propylene was about 3.7 cm^3

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[12] We believe the low OH values for $CD_3—CH=CH_2$ may be an artifact. The OH peak (Figure 3) is a weak peak on the side of a larger background peak; slight systematic shifts of the (larger) background peak would introduce large errors in the integrated intensity of the OH peak.

STP. In 6 hr 30 cm^3 of $CH_3—CH=CD_2$ isomerized. If the reaction is zero order (as it might be for a saturated surface), it will take about an hour to form a monolayer of $CHD_2—CH=CH_2$. Rereaction of this species, expected to be rapid, would cause the appearance of surface OD. Thus, if we had only a monolayer of $CH_3—CH=CD_2$ present, we would expect the half-time for equilibration of surface OH and OD's to be slightly more than 1 hr. The infrared data in Figure 4 suggest this half-time for $CH_3—CH=CD_2$ is about 80 ± 20 min, in rough agreement with the above analysis.

The composition of the surface product, in which more time for isomerization equilibrium has been allowed, approaches more closely than the gaseous product the computed "equilibrium" composition. Despite the fact that B would be expected to exceed C in the initial stages of the reaction, the amount of C in the products seems too low to explain by the kinetic sequence alone. Instead, the very low yield of C compared to B seems to require a sizable kinetic isotope effect for the formation of C *via* a 1,3 migration of deuterium.[13] This conclusion, although plausible in terms of the mechanism, should be regarded as tentative in the absence of a study of comparative rates of isomerization of $CH_3—CH=CD_2$ and $CD_3—CH=CH_2$.

Intermolecular Hydrogen Exchange. The deuterium distribution in the gaseous products in the propylene isomerization run shows that intermolecular hydrogen transfer accompanies the isomerization. Under conditions such that 70% of the propylene has isomerized, *i.e.*, undergone intramolecular hydrogen exchange, about 20% of the propylene has lost or gained deuterium due to intermolecular hydrogen transfer. We can express these results in a different way. If we assume the rate of both reactions is first order in the distance from equilibrium, the half-time for isomerization (based on disappearance of reactant) is 2.7 hr compared to about 11 hr for intermolecular deuterium transfer.

The rate of intermolecular transfer can also be studied by exchange studies of C_3H_6-C_3D_6 mixtures. Data for the exchange reaction are listed in Table III.

Table III. Intermolecular Hydrogen Exchange (%)

	Propylene[a]		Ethylene[b]	
Species	$t = 0$	$t = 1$ hr	$t = 0$	$t = 1$ hr
d_0	48.60	44.83	46.19	42.35
d_1	0.27	3.22	0.26	4.26
d_2		0.53		0.77
d_3		0.19	2.70	6.63
d_4		0.50	50.85	46.00
d_5	2.52	5.60		
d_6	48.60	45.03		
Av D/molecule	3.05	3.05	2.12	2.10

[a] The total pressure was 300 mm. [b] The total pressure was 230 mm.

If we assume the rate is first order in the distance from equilibrium for C_3H_6 and C_3D_6, we find that the half-time for this reaction is 9 hr, in fair agreement with the 11 hr obtained for the similar reaction with $CH_3—CH=CD_2$.

Ozaki, Ai, and Kimura[14] have reported a similar intermolecular exchange for ethylene. This reaction is not expected on the basis of infrared studies of ethylene on this catalyst, insofar as adsorption occurs without noticeable dissociation. We have accordingly checked to see if such exchange occurred on this catalyst; these data are also shown in Table III. The half-time for this exchange is 7 hr; if we multiply by $^{300}/_{230}$ to put it on the same pressure basis as propylene, we obtain a half-time of 9 hr. Thus, the intermolecular hydrogen exchange for ethylene is as rapid as that for propylene. Accordingly, it is not clear whether the intermediate in this reaction is the π allyl complex or the π-bonded propylene[7] which appears to be similar to adsorbed, "π-bonded" ethylene.

Addition of Deuterium to Propylene. Table IV summarizes the products of the reaction when deuterium reacts with propylene. Prior to this reaction a check run was made with ethylene; the activity of the catalyst, which was slightly sintered, was midway between that of ZnO-9 and ZnO-9S.[3] The ethane formed by reaction with deuterium over this catalyst was essentially pure dideuterioethane. Previous investigations on zinc oxide have shown no evidence of exchange of deuterium with ethylene during reaction, *i.e.*, the unreacted ethylene was 99.8% C_2H_4. The rate of reaction of deuterium with ethylene was about an order of magnitude faster than the reaction with propylene under comparable conditions.

Table IV. Products from Addition of Deuterium to Propylene[a,b]

	Hydrogen	Propane	Propylene	Propylene[c]
% d_0	1.9	12.2 (16)	84.4 (84)	49.9 (44)
% d_1	6.1	20.9 (33)	14.1 (15)	28.9 (39)
% d_2	92.0	55.6 (30)	1.6 (1)	15.5 (14)
% d_3		11.3 (16)		5.7 (2.5)
% d_4				
Av D/molecule	1.90	1.66	0.173	0.770

[a] A 90-min run at 25° with $C_3H_6:D_2$ = 122:608 mm gave 18.5% conversion. [b] Values in parentheses are values expected for random distribution of deuteriums with the stated overall deuterium content. [c] This is the chemisorbed propylene after the run which is removed from the catalyst by degassing 1 hr at 125°.

The reaction of propylene with deuterium clearly involves exchange of propylenes with deuterium (Table IV). The approximate half-time for this reaction is 14 ± 4 hr based on a reaction first order in the distance from equilibrium. The uncertainty represents the spread in values obtained when the calculation is based on gaseous "hydrogen" and propylene, respectively.

If the gas-phase deuterium (slightly diluted with hydrogen) is added molecularly to the propylene present (which has undergone some exchange), the

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[13] This conclusion appears to be at odds with the observation (Figure 4) that $CD_3—CH=CH_2$ and $CH_3—CH=CD_2$ approach the equilibrium OH and OD concentration at comparable rates. It should be recalled, however, that the data in Table II were obtained at propylene pressures of about 300 mm, whereas the pressure was essentially zero for the experiments depicted in Figure 4. Since the conditions of these experiments were not comparable, the disagreement may be more apparent than real.

[14] A. Ozaki, H. Ai, and K. Kimura, *Proc. Int. Congr. Catal., 4th, 1968*, **2**, 708 (1969). In a previous paper[3] we stated that this reference reported ethylene dimerization over zinc oxide. We were wrong; although the authors relate the exchange reaction to dimerization, they found no dimerization over zinc oxide: A. Ozaki, private communication.

deuterium content of the propanes would be between 2.0 and 2.23 deuteriums per molecule. The lower deuterium content of the propane (1.66) suggests that the reacting deuterium *on the surface* is greatly diluted by exchange with the π allyl prior to reaction. The facts that ir studies show no adsorbed hydrogen in the presence of propylene and that the isotopic analysis of chemisorbed propylene shows extensive exchange support this view. We should note, however, that although the distribution of deuterium in the propylenes approximates a random distribution for their deuterium content, the distribution of deuteriums in the propanes shows a preference for the dideuterio species. Thus, although considerable scrambling does occur in the product propanes, a preference for formation of the dideuterio species is still evident. Presumably this means that some gaseous deuterium reacts with propylene without first undergoing exchange.

If we assume the rate of addition of deuterium to propylene is first order in hydrogen, the half-time for addition is about 5 hr. This means the rate of addition of deuterium is a factor of 3 faster than exchange with propylene. This estimate, however, depends on mechanistic assumptions. We can compare the rates in still another way. For every propane molecule formed, 1.25 deuterium atoms appear in the propylene. Some of the hydrogen released on the surface by this exchange returns to the gas phase, but about one-quarter of this hydrogen ($\sim$0.30/propane formed) adds to form propane; largely because of the preferential addition of this surface hydrogen, the product propane contains only 1.66 deuteriums per propane molecule.

Conclusions. All of the reactions cited in the introduction as expected for a reactive π-allyl species were found to occur at comparable rates. Moreover, the intramolecular exchange occurs by a 1,3 shift and there is no evidence on the time scale of these experiments for exchange of the hydrogen attached to the center carbon atom. These data cannot be readily accommodated by a mechanism involving alkyl reversal but are the expected behavior for a π-allyl species. If we couple these results with the fact that addition of deuterium to propylene yields isotopic scrambling in both olefin and paraffin, as expected for a π allyl, whereas there is no such scrambling for ethylene, which cannot form an allyl species, the case is quite strong that the surface π allyl plays a major role in these reactions. This view is flawed by the occurrence of intermolecular hydrogen exchange for ethylene, for which we have no plausible interpretation, but we still feel it is valid to conclude that formation of the π allyl is an important step in all of these reactions. Such a species offers an attractive possible pathway for double-bond isomerization of higher olefins but, as yet, we have no data on this point.

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Kinetic Studies of Exchange between Metallic Mercury and Mercury Compounds in Solution. III

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Abstract: A new reaction procedure has been developed to extend the study of the isotopic exchange of organomercury compounds with a metallic mercury surface. This has made possible the investigation of the exchange of mercury diphenyl in a series of solvents and in the presence of surfactants. Activation parameters have been examined according to Leffler's theory and have been interpreted to indicate a difference of solvation between the transition and the ground states. A comparison has also been made between the rates of exchange of mercury diphenyl and phenylmercuric chloride with a mercury surface saturated with reactant. Both results confirm the previous postulate that the reaction proceeds *via* an SEi four-center reaction mechanism.

Reutov and coworkers[2] were the first to investigate the heterogeneous exchange of mercury and organomercury compounds in organic solvents

$$\mathrm{PhHgA} + \mathrm{Hg}^* \longleftrightarrow \mathrm{PhHg}^*\mathrm{A} + \mathrm{Hg}$$

where A = Ph or halogen.

Initially they concluded that the reaction rate was controlled by the rate of diffusion of the mercury from the metallic bulk of the surface. They therefore stirred the mercury at high speed causing it to break into droplets. Part I[3] in this series of papers drew attention to the difficulty of maintaining a constant surface area of the mercury, and hence a constant rate, during stirring. This difficulty was circumvented by rigorously defining

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(2) O. A. Reutov and G. M. Ostapchuk, *Dokl. Akad. Nauk. SSSR*, **117**, 826 (1957); O. A. Reutov and U. Tan-Tsei, *ibid.*, **117**, 1003 (1957); O. A. Reutov, P. Knoll, and U. Yan-Tsei, *ibid.*, **120**, 1052 (1958); A. N. Nesmeyanov, O. A. Reutov, and P. Knoll, *ibid.*, **118**, 99 (1958); O. A. Reutov and G. M. Ostapchuk, *Zh. Obshch. Khim.*, **29**, 1614 (1959).

(3) D. R. Pollard and J. V. Westwood, *J. Amer. Chem. Soc.*, **87**, 2809 (1965).