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Double Bond Migration, Geometric Isomerization, and Deuterium Distribution during Heterogeneous Catalytic Deuteration of Methyl Oleate

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Methyl *cis*-9-octadecenoate was deuterated over platinum and palladium catalysts. Saturates as well as *cis*- and *trans*-octadecenoates were separated for subsequent oxidative cleavage, gas chromatography, and mass spectrometry. The observed migration and geometric isomerization of double bonds, the distribution of deuterium along the carbon chain, and the presence of hydrogen and also deuterium on the catalyst surface are collated by an extension of the Horiuti-Polanyi mechanism. These reactions were simulated by digital computer calculations of the proposed model.

INTRODUCTION

Methyl oleate, with its cis double bond located in the middle of a normal C_{18} chain and with an ester group distinguishing one end of the molecule, is a particularly useful structure for the study of catalytic deuteration. It has long been known that double bond migration and cis–trans isomerization take place during hydrogenation of methyl oleate (*1*, *2*). More recently, extensive exchange has been observed in both methyl oleate and methyl stearate when deuterium is substituted for hydrogen (*3*, *4*).

The present experimental work was planned so that isomerization, migration, and exchange under one set of conditions could be observed and compared for platinum and palladium catalysts. The results have been simulated by a computer for a model based on the Horiuti-Polanyi mechanism.

EXPERIMENTAL

The design of experiments is given in Fig. 1. Deuterations were conducted in a 125-ml Erlenmeyer flask with a slightly rounded bottom to give better stirring with a magnetic bar. The flask was immersed in a constant temperature bath at 40°C, was fitted with a rubber septum outlet through which samples could be removed with a needle and syringe, and was connected to vacuum pumps through a stopcock and through capillary tubing to a gas burette.

Oleic acid was prepared from olive oil by the method of Rubin and Paisley (*5*) and esterified with methanol.

Catalysts used were Baker and Company, Inc.,* 5% platinum on carbon and 5% palladium on carbon without special treatment.

Deuterations were carried out by placing 30 g of methyl oleate in the flask with 0.25% platinum or 0.068% palladium—concentrations chosen so that both reactions would take about 3.5 hr for total reduction. Liquid and gas samples were taken at 20%, 40%, 60%, 80%, and 100% of complete reduction. These gas samples represent the head space in the reaction flask—about 100 to 125 ml—which is

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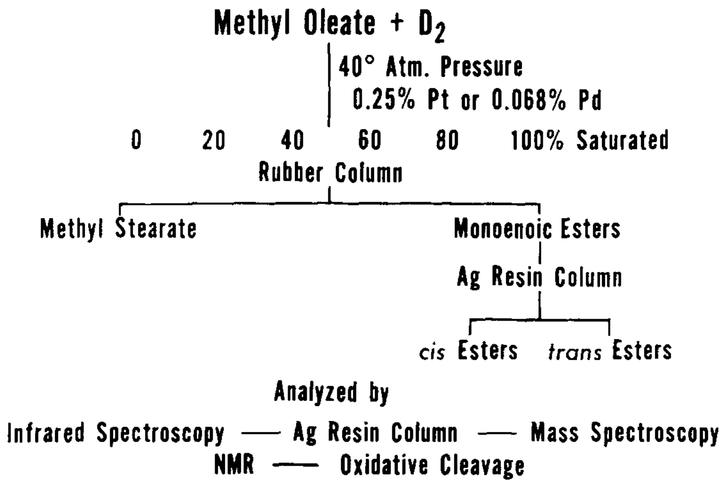

FIG. 1. Design of deuteration experiments and analysis of products.

isolated from deuterium in the gas burette by capillary tubing. After each gas sample was removed, the reaction flask was evacuated and filled with fresh deuterium.

With palladium, three duplicate runs were made and corresponding liquid-phase samples from each run were combined to provide more material for processing and analysis; an additional liquid sample also was taken at 10% reduction.

Samples were separated by chromatography on a rubber column (*6*) into stearate and monoene fractions, and the monoenes were separated into cis and trans fractions on a silver resin column (*7*). The output of the chromatographic columns was monitored by a differential refractometer. The areas under the curves provided values for cis and trans contents of monoene, as also did the weights of recovered material.

Infrared spectrometry was used to determine the percentage isolated trans in the monoene fractions by utilizing the absorption band at 965 cm^{-1} according to the method of Shreve *et al.* (*8*).

Analytical data are given in Table 1 for platinum and palladium reductions.

Double bond positions shown in Figs. 2 and 3 were determined by periodate–permanganate oxidative cleavage followed by gas chromatography of the methyl mono- and dibasic acids formed during

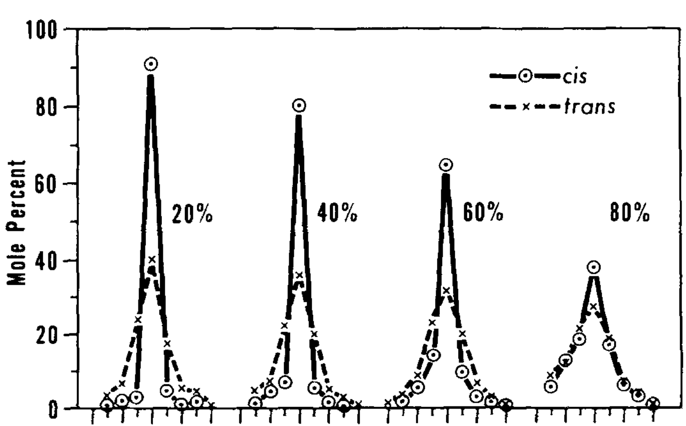

FIG. 2. Distribution of double bonds in *cis*- and *trans*-octadecenoates as a function of degree of reduction (platinum catalyst).

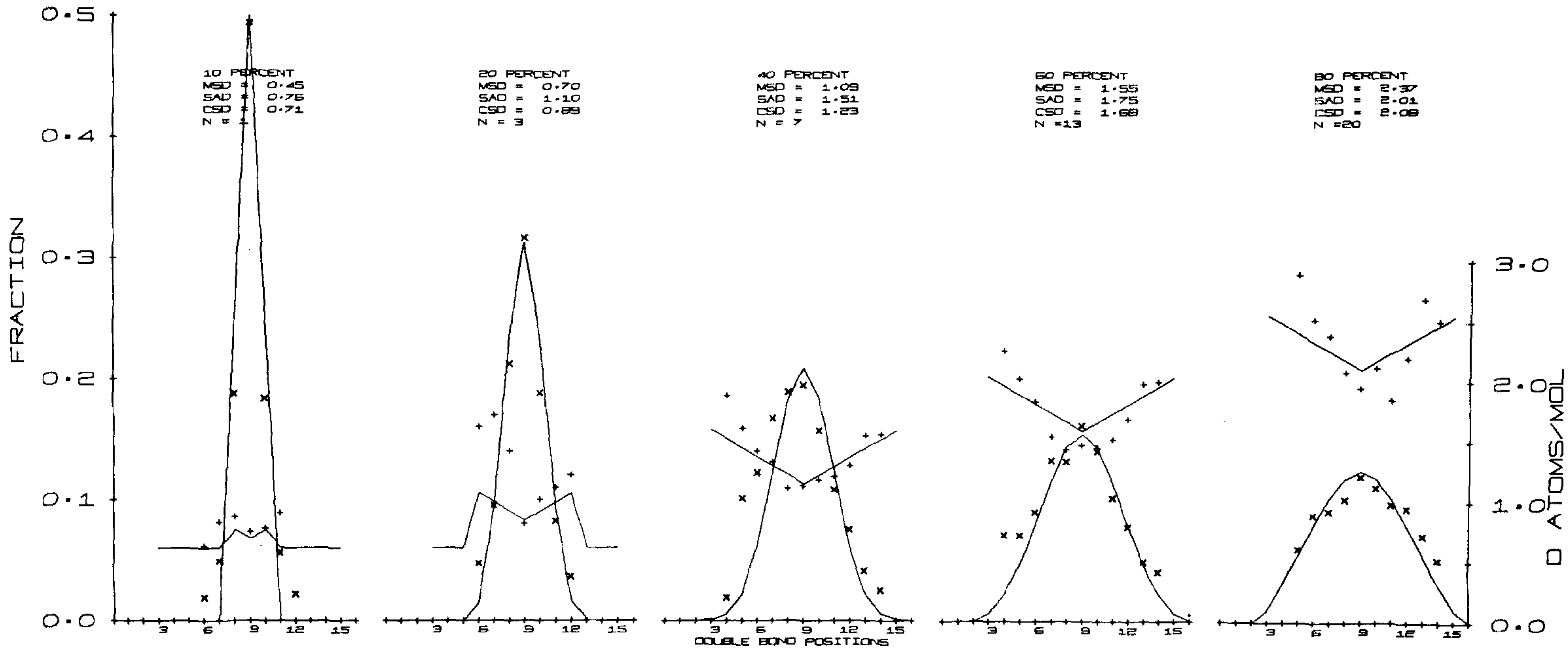

FIG. 3. Distribution of double bonds in *cis*- and *trans*-octadecenoates as a function of degree of reduction (palladium catalyst). Curves are computer drawn simulation of expanded model of Fig. 6. N, exponent of binomial expansion; SAD, summation of analytically determined deuterium; CSD, calculated summation of deuterium; MSD, mass spectrometrically deuterium determined from parent peak.

TABLE 1

Deuteration of Methyl Oleate

Analysis	Platinum catalyst					Palladium catalyst					
D_2 uptake, % of saturation	20.0	40.0	60.0	80.0	98.5	10.0	19.9	39.9	59.9	79.9	98.3
Stearate, GLC (%)	19.2	40.0	60.1	80.7	100	8.0	16.8	37.3	58.2	79.6	100
Trans in monoene, IR (%)	22.2	41.2	55.0	55.2	—	66.1	70.8	69.1	64.1	55.1	—
Trans in monoene, Ag resin (%)	22.1	46.2	64.2	79.7	—	69.4	83.4	83.0	82.0	79.8	—
Trans in *trans* monoene, IR (%)	85.0	82.6	75.8	66.5	—	91.9	92.9	79.9	78.0	65.0	—
D atoms per molecule, mass spec.											
Stearate	1.40	1.52	1.71	1.95	2.36	0.87	0.93	1.24	1.50	1.82	2.4
Cis monoene	0.48	0.62	1.23	2.01	—	0.34	0.66	1.01	1.61	2.42	—
Trans monoene	1.00	1.11	1.42	1.97	—	0.49	0.67	1.10	1.53	2.36	—
Stearate, differential	1.4	1.6	2.1	2.7	4.1	0.87	0.97	1.5	2.0	2.7	4.6
Isotopic % of deuterium on catalyst	42.0	45.0	53.0	48.0	91.0	27.0	21.0	31.0	32.0	38.0	90.0

TABLE 2

Deuterium Content of Cleaved Products—Platinum Catalyst[a]

	Cis					Trans			
Length carbon chain	Reduction (%)				Length carbon chain	Reduction (%)			
	20	40	60	80		20	40	60	80
Monobasic acids									
7	—	—	—	—	7	—	—	0.45	—
8	0.18	—	—	—	8	0.13	0.26	0.30	0.48
9	0.09	0.12	0.22	0.1	9	0.15	0.20	0.29	0.51
10	0.39	0.48	0.67	—	10	0.37	0.47	0.60	0.83
11	—	—	—	—	11	—	0.77	0.97	1.24
12	—	—	—	—	12	1.05	—	—	1.75
13	—	—	—	—	13	1.60	—	—	—
Dibasic acids									
6	—	—	—	0.40	6	0.34	0.24	0.26	0.21
7	—	—	0.19	0.35	7	0.14	0.12	0.24	0.23
8	—	—	0.18	0.24	8	0.089	0.12	0.15	0.28
9	0.094	0.086	0.35	0.19	9	0.081	0.13	0.26	0.33
10	—	—	—	—	10	0.27	0.30	0.41	0.77
11	—	—	—	—	11	0.58	0.60	0.72	1.25
12	—	—	—	—	12	—	0.94	1.25	1.89

[a] Atoms of deuterium per molecule.

cleavage (*9*). The methyl esters of the cleaved products were also trapped from gas-liquid chromatographic columns and examined for deuterium content by mass spectrometry. Results are given in Tables 2 and 3.

Composition of the gas samples as determined with a Bendix time-of-flight mass spectrometer is given in Table 4.

Results and Discussion

The reductions described in this paper were carried out under conditions typical of those often used for hydrogenating oils or other fatty esters in the laboratory. Under these conditions—atmospheric pressure, 40°C, magnetic stirring for agitation, and catalyst concentration such that approximately equal reaction times of about 3.5 hr were required for both platinum and palladium—the catalyst would be expected to be deficient in deuterium and hydrogen so that cis–trans isomerization and bond migration would be favored more than under conditions producing greater catalyst coverage. Also, since palladium has a greater tendency than platinum to effect isomerization under a wide range of conditions, the differences between the two catalysts are probably greater than they would be with greater amounts of deuterium and hydrogen on the catalyst surface.

Data for platinum catalysis given in the first two lines of Table 1 verify that the degree of deuteration of samples controlled manometrically is that found by GLC. Infrared spectroscopy (line 3) indicates that geometric isomerization from the cis to the trans configuration increases as deuteration proceeds up to 80% reaction; but the fourth line, calculated by measuring areas under the refractometric curves from chromatograms on Ag resin, reveals a much higher degree of isomerization at each sampling period. Line 5 is the percentage trans found by IR in the pure trans monoene from the chromatographic column and shows that the deuterium at the double bond is shifting the absorption away from the 965-cm^{-1} band where the percentage trans is measured. While these data prove that the IR band at 965 cm^{-1} cannot be used for the quantitative trans measurements, they do disclose an increase of deuterium on the double bond carbons as reaction proceeds.

TABLE 3

METHYL ESTERS OF CLEAVED OCTADECENOATES—PALLADIUM CATALYST[a]

	Cis					Trans				
	Reduction (%)					Reduction (%)				
Length carbon chain	10	20	40	60	Length carbon chain	10	20	40	60	80
					Monobasic acids					
6	0.10	—	0.18	—	6	—	0.19	0.17	0.37	—
7	0.10	0.22	0.26	0.48	7	0.29	0.11	0.23	0.27	0.33
8	0.14	0.28	0.27	0.44	8	0.39	0.16	0.21	0.34	0.51
9	0.13	0.21	0.31	0.57	9	0.19	0.15	0.26	0.49	0.68
10	0.18	0.23	0.42	0.67	10	0.31	0.23	0.37	0.51	0.96
11	0.21	0.38	0.59	0.91	11	0.61	0.37	0.58	0.69	1.18
12	—	0.54	0.91	1.12	12	—	0.57	0.68	0.97	1.43
13	—	—	1.28	1.44	13	—	—	0.86	1.16	1.81
14	—	—	—	—	14	—	—	1.13	1.39	—
					Dibasic acids					
6	—	—	0.18	0.25	6	—	0.13	0.18	0.25	0.49
7	0.07	0.11	0.15	0.25	7	0.10	0.07	0.13	0.25	0.60
8	0.043	0.059	0.19	0.35	8	0.053	0.055	0.13	0.31	0.53
9	0.043	0.11	0.28	0.40	9	0.12	0.10	0.25	0.37	0.67
10	0.042	0.27	0.30	0.66	10	0.26	0.26	0.35	0.50	1.01
11	0.11	0.29	0.57	0.80	11	0.24	0.45	0.36	0.64	0.93
12	—	0.24	0.69	1.00	12	—	—	0.51	0.72	1.27
13	—	—	—	1.26	13	—	—	0.76	1.04	1.47
14	—	—	—	1.39	14	—	—	0.77	1.06	1.91

[a] Atoms of deuterium per molecule.

TABLE 4
DEUTERATION OF METHYL OLEATE—COMPOSITION OF GAS PHASES AND CALCULATED D ON CATALYST SURFACE (ATOM %)

Catalyst	Gas composition	D_2 uptake, % of saturation				—
		20	40	60	80	100
Pt	H_2	4.8	5.8	5.3	7.5	2.9
Pt	HD	19.4	24.3	25.4	28.8	25.7
Pt	D_2	75.8	69.9	69.3	63.7	71.3
Pt, calc. % D on cat. surface		69.9	70.6	73.2	68.8	84.1
Pd	H_2	5.7	5.2	4.6	4.0	7.0
Pd	HD	9.9	9.3	10.0	8.2	23.0
Pd	D_2	83.8	84.8	84.8	87.4	69.4
Pd; calc. % D on cat. surface		48.9	49.3	54.3	53.4	70.2

The number of deuterium atoms per molecule (lines 6–8), calculated from mass spectral data similar to those in Fig. 4, shows that the deuterium content increases with degree of saturation of the hydrogenation mixture. As expected, the starting cis monoene has the lowest deuterium content; the trans monoene that has necessarily experienced at least one absorption and desorption has an intermediate value; and the stearate or saturated ester has the highest. One observes that the stearate does not contain two atoms of deuterium more than the cis and trans monoenes; instead the stearate contains much less than two. These results are explicable only if it is assumed that a mixture of hydrogen and deuterium is present on the catalyst surface. This assumption is supported by data to be presented later.

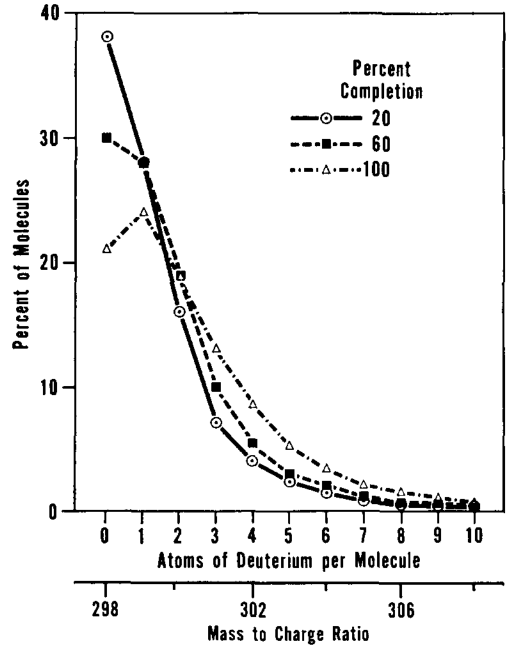

FIG. 4. Mass spectra, parent peak region, for methyl octadecanoate from methyl oleate deuterated over Pt catalyst.

Palladium catalysis (Table 1) differs from platinum in the rate at which the equilibrium mixture of cis and trans isomers is reached and in the deuterium contents of stearate and trans monoene fractions. Calculations of the last two lines of Table 1 will be developed below.

Double bond distributions for cis and trans fractions of the increasingly saturated mixture are shown in Fig. 2 for platinum catalysis. The methyl octadecenoate starting material was all cis configuration with the unsaturation at the 9-position. Initially, the cis monoenes display less bond migration than corresponding trans monoenes; however, by the time the mixture is 80% saturated the bond distribution in the cis and trans fractions is indistinguishable.

Comparable results for bond distribution with the palladium catalyst are given in Fig. 3. They differ from those with platinum in showing indistinguishable bond distribution for cis and trans fractions at the 20% level of saturation rather than the 80% level. Moreover, the bonds are scattered more widely with the Pd catalyst than for comparable degrees of saturation with a Pt catalyst.

Deuterium contents of the cleaved and isolated monobasic and dibasic esters from the cis and trans monoenes were determined by examining the parent peak (P) and the P-31 regions of mass spectra. Because of the nature of the oxidative cleavage reaction, olefinic deuterium atoms are, of course, lost to the aqueous solvent. As expected for each mono- and dibasic acid, the deuterium content for platinum catalysis (Table 2) increases as the degree of saturation of the mixture increases (reading left to right) and as chain length increases (reading down each column). Therefore, the longer the reaction time, the more the deuteration; also, the greater the migration of the double bond from its original 9-position, the greater the deuterium content of the cleaved fragments and of the parent monoenoic isomer.

Comparable data for the Pd catalyst experiments are given in Table 3. They differ primarily in being more complete and extending over a broader range of carbon chain lengths.

At first inspection, the data of Fig. 4 (Pt) for the mass spectrum of methyl octadecenoate in the parent peak region seem anomalous. For example, it seems surprising at the 20% saturation level that the most prominant molecular species of a catalytic deuteration should have no deuterium atoms. As previously noted this result can occur only if a high proportion of isotopes on the catalyst surface are hydrogen despite the 100% deuterium introduced into the gas phase. As catalytic deuteration proceeds, apparently the numbers of molecular species with increasing deuterium contents are also increasing.

The corresponding spectra for the Pd catalyst show even larger proportions of nondeuterated stearate, resulting from a greater H/D ratio on the catalyst surface.

Estimates of the ratio of hydrogen to deuterium on the catalyst surface have been made in two ways: (1) by calculations based upon the mass spectrometrically determined HH, HD, and DD contents of the gas phase (Table 4) and (2) by determinations of the incremental increase in deuterium content of the saturates coming from the unsaturated precursor (Tables 2 and 3).

In calculations by a method based on data in Table 4, the deuterium in the gas phase is considered to be made of two parts: (1) one which has just passed through the capillary from the gas burette into the reaction flask and has never been in contact with the catalyst and (2) the other, which has been equilibrated on the catalyst surface with hydrogen from the ester and released again to the gas phase along with H_2 and HD. Then,

$$\underset{\text{(Released from catalyst)}}{H_2(\%) + HD(\%) + D_2(\%)} + \underset{\text{(Unadsorbed)}}{D_2(\%)} = \underset{\text{(Analysis of gas)}}{H_2(\%) + HD(\%) + D_2(\%)}$$

Values for unadsorbed D_2 may be chosen so that the other three terms on the left side of the equation above correspond to the ratio $H_2/HD/D_2$ for an equilibrium mixture corrected for isotope effect. It is assumed that the percentages of H and D corresponding to this equilibrium mixture corresponds to the percentages of H and D on the catalyst surface.

The calculated values of atom percent of deuterium in the equilibrium mixture from Table 4 are also given in Table 5. Except at 100% reaction these data show about 30% H, 70% D on the platinum catalyst, and 50% H, 50% D on palladium. The values at 100% completion of reaction have little significance. When no more hydrogen is exchanged from the ester and when no more deuterium enters from the burette, the remaining gas in the reaction flask will approach equilibrium. These values, then,

TABLE 5

Isotopic Percentage of Deuterium on Catalyst

Catalyst	Level of deuteration					
	10	20	40	60	80	100
Pt[a]	—	69.9	70.6	73.2	68.8	84.1
Pt[b]	—	42.0	45.0	53.0	48.0	91.0
Pd[a]	—	48.9	49.3	54.3	53.8	70.2
Pd[b]	27	21.0	31.0	32.0	38.0	90.0

[a] Gas analysis.

[b] Product analysis.

reflect the extent to which this equilibrium had been approached when the gas sample was taken.

The hydrogen–deuterium ratio on the catalyst may also be assessed by method 2 using lines 6, 7, and 8 of Table 1. One first calculates the deuterium composition of the new stearate formed in each 20% of reaction by subtracting the deuterium in stearate in the previous fraction from the present total to give the differential deuterium compositions shown in line 9 for the newly formed stearate. One can calculate the composition of the gas on the catalyst to convert the monoene to stearate for each 20% increment. These values are listed as isotopic percent of deuterium on catalyst in Table 1. The concentration of deuterium on the catalyst is as low as 21% with palladium and 42% with platinum. One would expect the deuterium content to be lowest in the beginning since the concentration of monoene is highest and the available hydrogen on the monoene is highest then. The deuterium content goes up toward the end of the reaction because there is less monoene to exchange hydrogen, much of the hydrogen on the monoene has already been exchanged for deuterium, and thereby the available hydrogen is reduced.

As summarized in Table 5, the values for isotopic percent deuterium, shown in Table 4 as determined by gas analysis, agree in relative values and in the direction of the trend with values calculated from product analyses in Table 1, but disagree in absolute values, probably due to assumptions made in the calculations, to isotope effects in gas transfer to the catalyst, in adsorption on the catalyst, or in the addition to the double bond, or to a higher concentration of H on the catalyst in the immediate vicinity of the ester.

Observations herein are consistent with the classical Horiuti-Polanyi mechanism involving the alternation of mono- and diabsorbed species. The observations are collated by an extension of this theory formulated by Smith and Burwell *(10)*, and are adapted in Fig. 5 *(4)* specifically for the deuteration of methyl oleate. In this form, Fig. 5 serves to show bond migration from the 9, 10- to the 10, 11-position in methyl oleate with a concomitant geometric isomerization of the double bond from cis to trans and an exchange of carbon-bonded hydrogen for deuterium. Unsaturated esters and gaseous deuterium are adsorbed on the catalyst surface; as the esters pass repeatedly between the diadsorbed and monoadsorbed species, hydrogen from the esters is exchanged with deuterium. The exchange is responsible for the deuterium found in monoenoic esters, the presence of 10 atoms of deuterium in individual monoenoate and stearate molecules, and the presence of hydrogen on the catalyst surface. Hydrogen exchanged from the ester to the catalyst may also add to unsaturated esters to form stearate with only one or no deuterium, or it may be desorbed to the gas phase as H_2 or HD. Thus H and D at the reactive positions of the monoene and in the gas phase are all in dynamic equilibrium on the catalyst surface.

Also, as monoenoic esters alternate between the monoadsorbed and diadsorbed species, double bonds isomerize to give cis, trans mixtures (Table 1). If we consider that the monoenes have an equilibrium trans value of 80%, then for platinum at 20% reduction, 22.1/80 or about 28% of the monoene has been adsorbed on the catalyst and desorbed at least once and the rest has not yet been adsorbed on the catalyst. Similarly, at 40% reduction 58% has been desorbed and at 60% reduction 80%. At 80% reduction (or the equilibrium cis, trans mixture) essentially all the monoene has been in contact with the catalyst at least once. With palladium, the trans value has reached equilibrium at 20% reduction and all the esters may be considered to have been desorbed from the catalyst at least once. Since both the platinum and palladium systems were mechanically identical, with same temperature, stirring, and viscosity, the methyl oleate molecules must have had the same opportunity for collision on both catalysts. It follows then that palladium chemically adsorbs and desorbs much more rapidly than platinum *(11)* or that once adsorbed

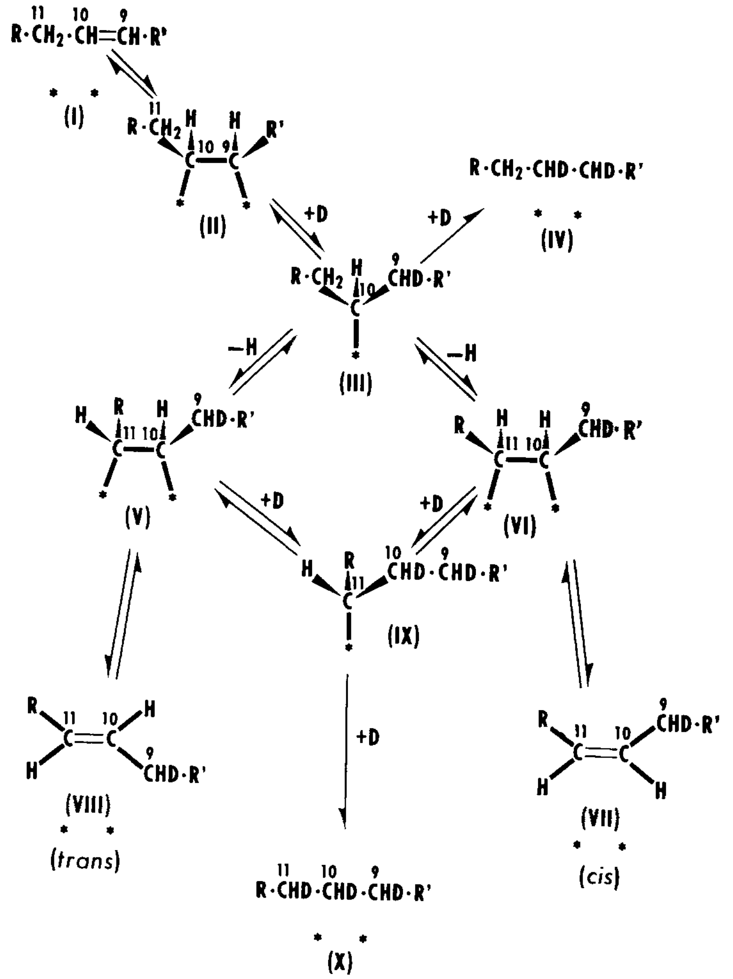

FIG. 5. Extension of Horiuti-Polanyi mechanism to show geometric isomerization of double bonds and deuterium exchange and addition.

the olefin on palladium undergoes more alternations between mono- and diadsorbed species than it does on platinum.

The model given in Fig. 6 is similar to Fig. 5 but illustrates further concepts and assumptions made in the subsequent digital computer simulation of catalytic deuteration. These assumptions are that each movement outward from the central bond position through mono- and diabsorbed species results in the absorption of one deuterium atom, whereas each inward movement or return toward the central position results in the statistical loss of one-half a deuterium atom.

This model illustrates both the binomial process of distribution of double bonds and the exchange of deuterium as successive alternations of mono- and diadsorbed species take place. The scheme has been simulated and extended by a digital computer. The resultant calculations for palladium hydrogenation experiments previously shown are plotted as a theoretical curve in Fig. 3. Distributions for 10%, 20%, 40%, 60%, and 80% saturation correspond to exponents of the binomial expansions of 1, 3, 7, 13, and 20, respectively. These exponent values interpreted in light of Figs. 5 and 6 for the Horiuti-Polanyi mechanism are the average number of alternations between mono- and di-

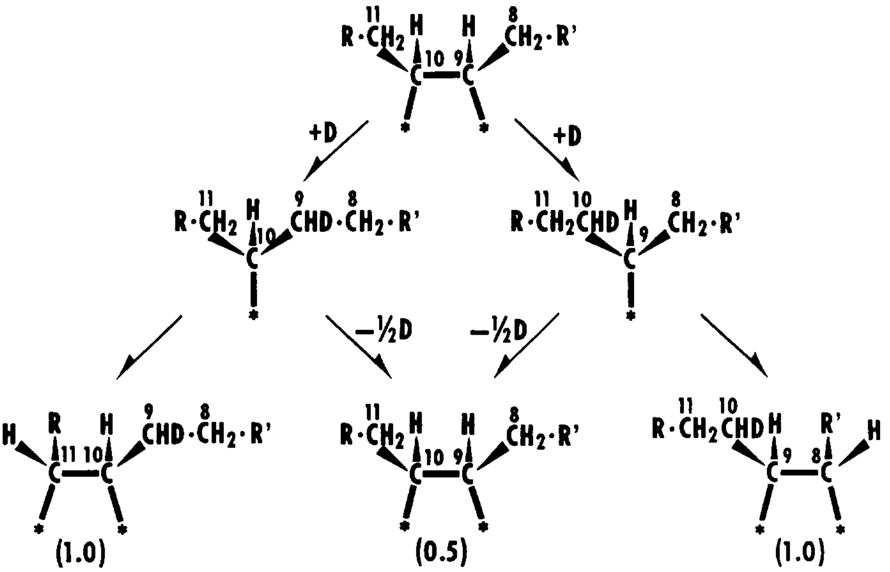

FIG. 6. Model to show bond migration and deuterium exchange based on Horiuti-Polanyi mechanism.

adsorbed species that the unsaturated molecules have experienced up to that point of the reaction.

For the simulation of platinum catalysis, the exponents corresponding to 40%, 60%, and 80% saturation are 1, 2, and 4, respectively, and reflect the lower tendency of platinum to move double bonds for comparable degrees of reaction compared to palladium. These results may be interpreted in terms of the relative rates of saturation and positional isomerization for the two catalysts; i.e., the rate at which in Fig. 5 species (III) goes to (IV) vs. the rate at which (III) goes to (V), (VI), and (IX) in the diamond arrangement of reactions. Reactions involving the alternation of adsorbed species and causing isomerization are more significant for palladium catalysis than for platinum catalysis.

There exists no necessary conflict between the observations of average numbers of alternations of mono- and diadsorbed species just described and the interpretations of trans results by Ag resin given earlier. With platinum at 40% saturation the average number of alternations of one corresponds to a minimum of 58% of molecules having been adsorbed and desorbed from the catalyst surface as determined by Ag resin chromatography; at 60% saturation, two average alternations correspond to a minimum of 80% of molecules adsorbed and desorbed, and at 80% saturation four average alternations correspond to essentially 100% of the molecules coming in contact with the catalyst surface.

With palladium catalysis, 10% saturation corresponds to approximately one alternation and a minimum of 87% of the molecules having been adsorbed and desorbed from the catalyst surface. Twenty percent saturation corresponds to three alternations and essentially 100% of catalyst contact. Thus even on dissimilar catalyst surfaces, the number of molecules adsorbed and desorbed as determined by Ag resin chromatography and the number of alternations of mono- and diadsorbed species as determined from the analysis of this model have comparable values.

The straight lines of Fig. 3 are the distributions of deuterium with bond position calculated on the simple assumptions given above; namely, movement of the bond position outward from the center causes the absorption of one atom of deuterium, and movement of the bond one position toward the central position results in a loss of one-half deuterium atom. The actual calculations include the experimental factor for the deuterium to hydrogen ratio; namely, three-tenths for palladium.

If the theoretical deuterium content for species is multiplied by the theoretical percentage which that species makes up of the theoretical binomial distribution and if these products are summed, the calculated summation of deuterium (CSD) given in Fig. 3 is obtained. This value may be compared to the summation of analytically determined deuterium (SAD) which is the corresponding summation of products for the percentage each isomer comprises of the fraction times the deuterium content of each isomer as measured on the oxidatively cleaved fragments by mass spectrometry and as corrected for the loss of olefinic deuterons during oxidation. The deuterium contents for the total fraction determined directly from mass spectrometric data (MSD) in the parent peak region are also given. The agreement of the calculations made with these admitted approximations (CSD) to the two experimentally measured values (SAD, MSD) do encourage further and more detailed simultations of this mechanism on a digital computer. At present it would appear that observations of deuterium absorption and exchange and of double bond migration and isomerization are consonant with premises of the Horiuti-Polyanyi mechanism.

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