Application of Microwave Spectroscopy to the Mechanism of Hydrogen–Deuterium Exchange in Propene by Homogeneous Catalysts

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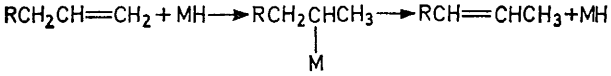
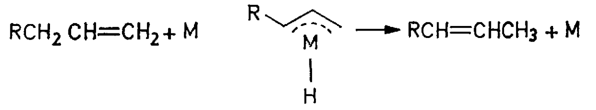
Quantitative microwave analyses of $[^2H_1]$propenes formed by deuterium exchange of propene with CH_3OD by homogeneous catalysts of platinum, rhodium, and nickel are reported. The results permit a clear choice of the metal hydride addition–elimination mechanism over the π-allyl mechanism. Secondary isotope effects in the β-elimination of MH from the intermediate 1-deuterio-2-metallo-propane are in good agreement with a calculated value of k_H/k_D = 1·18. The relationship of the propene results to deuteriation/isomerization studies on but-1-ene is discussed.

OLEFIN isomerization, involving migration of a double bond along a hydrocarbon chain, is an important part of a variety of catalytic reactions, including hydrogenation,[1] hydroformylation,[2] hydrosilation,[3] and polymerization.[4] Although a number of mechanisms have been suggested, the two most common [5] are the metal hydride addition–elimination mechanism (1) and the π-allyl mechanism (2), where M denotes a transition metal and



$$RCH_2CH{=}CH_2 + MH \longrightarrow RCH_2\underset{\displaystyle M}{\underset{|}{C}}HCH_3 \longrightarrow RCH{=}CHCH_3 + MH \quad (1)$$



(2)

ancillary ligands. These ligands might be tertiary phosphines in a discrete transition-metal complex or other metal atoms in the surface of a heterogeneous catalyst. Both paths involve M–H bonds;[6] the question is whether C–H bonds form or break in the first step. In both cases replacement of M–H for M–D can lead to deuteriation of the hydrocarbon chain, and deuteriation studies have been used extensively for elucidating the details of the isomerization–exchange reaction. Mass spectrometry is commonly used to establish the amounts of various deuteriated species $[^2H_0]$, $[^2H_1]$, and $[^2H_2]$, *etc.*, but cannot reliably establish the positions of deuteriation within the molecules. I.r. and n.m.r. spectroscopy have been used to establish the location of deuterium, but both methods suffer from a lack of sensitivity and quantitative reliability when used to analyse mixtures of partially deuteriated molecules.

Microwave spectroscopy has extremely high resolution and has recently been used for precise quantitative analysis. Its utility in exploring mechanisms in heterogeneous catalytic reactions has been reported by a number of groups, particularly Hirota and his co-

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[1] (*a*) E. N. Frankel, E. A. Emken, H. Itatani, and J. C. Bailar, *J. Org. Chem.*, 1967, **32**, 1447; (*b*) D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2610.

[2] D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3133.

[3] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1967, **89**, 1640.

[4] (*a*) C. S. Marvel and J. R. Rogers, *J. Polymer Sci.*, 1961, **49**, 335; (*b*) R. Cramer, *J. Amer. Chem. Soc.*, 1965, **87**, 4717.

[5] R. Cramer, *J. Amer. Chem. Soc.*, 1966, **88**, 2272.

[6] A review of the role of transition metal hydrides in homogeneous catalysis by C. A. Tolman has recently appeared in 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, Inc., New York, 1971, ch. 6.

workers.[7,8] Here we report on the application of microwave spectroscopy to the analysis of [$^{2}H_{1}$]propene produced by homogeneous catalysts containing platinum, rhodium, and nickel, previously shown [9] to be active in the isomerization/deuteriation of butenes.* Our results, which represent the first application of microwave spectroscopy to homogeneous catalytic systems, are considerably more precise than those reported earlier for the heterogeneous systems and confirm the earlier conclusions [9] about the importance of the metal hydride addition–elimination mechanism. The accuracy of our measurements permits us to determine secondary isotope effects in the metal hydride elimination reactions and to estimate relative rates of anti-Markovnikov and Markovnikov metal deuteride addition. The relationship of our results to the isomerization/deuteriation of butenes is discussed.

TABLE 1

Analysis of propene–propane mixtures after deuterium exchange reactions

Catalyst	Sample	Reaction time (h)	% Propene	[$^{2}H_{n}$]Propene analysis							% Propane	[$^{2}H_{n}$]Propane analysis				
				$n = 0$	1	2	3	4	5	6		$n = 0$	1	2	3	4
Pt	1	3·5	98·5	75	23	2·5	0·1				1·5	46	34	16	4	
	2	7·0	96·9	64	30	5	0·4	0·1			3·1	28	32	30	9	1
Rh	1	0·1	99·7	55	32	11	2·5	0·4	0·1		0·3 [a]					
	2	0·3	99·6	27	31	24	12	4·5	1	0·1	0·4 [a]					
Ni	1	1·5	95·2	89	10	0·6	0·1				4·8	93	7	0·5		

[a] Too little sample for accurate mass spectral analysis.

EXPERIMENTAL

The preparations of (acac)Rh(C_2H_4)$_2$ [11] and Ni[P(OEt)$_3$]$_4$ [12] are described in the literature. Other materials were purchased commercially and used without further purification. The propene was research grade and the CH_3OD (99% ^{2}H) was obtained from Chemi-Standards, Inc. Anhydrous $SnCl_2$ was prepared by heating the hydrate under vacuum to constant weight.

After the exchange reactions, the propene and propane formed were separated by preparative gas chromatography using an 8-ft column of 25% ester amide on Gas Chrom RA at a temperature of 0 °C and a He flow rate of 240 ml min^{-1}.

Mass spectra of the fractions were obtained on a CEC-21-103-C mass spectrometer. Statistical corrections were made for ^{13}C and deuterium but no corrections were made for kinetic isotope effects on the fragmentation patterns. Microwave spectra were obtained with a Hewlett–Packard 8460 A spectrometer. The methods of measurement and analysis of errors are described in detail elsewhere.[13]

Deuterium Exchange Reactions.—The deuterium exchange reactions were carried out in CH_3OD at 0 °C. The weighed catalyst (*ca.* 0·2 mmol) and CH_3OD (2 ml, 50 mmol) were charged under nitrogen into a flask (50 ml) equipped with a Teflon-coated magnetic stirring device. The contents of the flask were frozen in liquid nitrogen and degassed by successive pumping, thawing, and refreezing. DCl (*ca.* 0·8 mmol) and propene (103 ml, 4·2 mmol) were then condensed into the flask which was then warmed to 0 °C with vigorous stirring. After a measured time the reaction was quenched by immersing the flask in liquid nitrogen. Volatile gases were transferred to liquid nitrogen-chilled stainless-stell bombs by allowing the reaction mixture to warm gradually to 0 °C. Typical reactions are described below.

(1) $PtCl_4/SnCl_2/DCl/H_2/CH_3OD$. To $PtCl_4$ (0·10 g, 0·3 mmol) and anhydrous $SnCl_2$ (0·23 g, 1·2 mmol) was added CH_3OD (2 ml, 50 mmol). After degassing, DCl gas (16·5 ml, 0·7 mmol), H_2 (5·5 ml, 0·22 mmol), and propene (103 ml, 4·2 mmol) were condensed in. The homogeneous red-brown solution was vigorously stirred for 7·0 h at 0 °C before being quenched in liquid nitrogen.

(2) (acac)Rh(C_2H_4)$_2$/DCl/CH_3OD. To (acac)Rh(C_2H_4)$_2$ (0·025 g, 0·1 mmol) in CH_3OD (2 ml) was added DCl (25·2 ml, 1·0 mmol). The catalyst was activated by warming to 25 °C for 5 min, during which time the solution changed from yellow to deep orange. The flask was chilled in liquid nitrogen and propene (103 ml) was condensed in. The flask was quickly warmed to 0 °C with vigorous stirring and rechilled after 6 min.

(3) Ni[P(OEt)$_3$]$_4$/DCl/CH_3OD. To Ni[P(OEt)$_3$]$_4$ (0·145 g, 0·2 mmol) in CH_3OD (2 ml) was added DCl (12·6 ml). After propene (103 ml, 4·2 mmol) had been added, the flask was warmed to 0 °C, causing the nickel compound to dissolve to give a light-yellow solution. The reaction was quenched after 1·5 h.

After the deuterium exchange reactions, the samples were analysed for propene and propane by gas chromatography (g.c.); samples of the gases were saved for later mass spectral and microwave analysis for deuterium. Table 1 shows the results of g.c. and mass spectral analysis.

RESULTS AND DISCUSSION

Exposure of propene to CH_3OD solutions of the homogeneous catalysts at 0 °C led to extensive introduction of deuterium and to the formation of small amounts of deuteriated propane, as shown by the data in Table 1.

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* Two of these systems, (acac)Rh(C_2H_4)$_2$/HCl[5] [acac = acetylacetonate] and Ni[P(OEt)$_3$]$_4$/H^{+},[10] have been the subjects of extensive mechanistic studies.

[7] (*a*) K. Hirota, Y. Yasuda, S. Teratani, and N. Yoshida, *Z. Phys. Chem.* (*Frankfurt*), 1970, **71**, 195; (*b*) T. Ueda, J. Hara, K. Hirota, S. Teratani, and N. Yoshida, *ibid.*, 1969, **64**, 64; (*c*) K. Hirota, N. Yoshida, S. Teratani, and S. Saito, *J. Catalysis*, 1969, **15**, 425; (*d*) K. Hirota, N. Yoshida, S. Teratani, and Y. Kitayama, *ibid.*, 1969, **13**, 306; (*e*) K. Hirota and Y. Hironaka, *ibid.*, 1965, **4**, 602.

[8] Y. Sakurai, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, 1971, **67**, 3094.

[9] R. D. Cramer and R. V. Lindsey, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 3534.

[10] C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94**, 2994.

[11] R. D. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

[12] R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, 1964, **3**, 1062.

[13] L. H. Scharpen, R. F. Rauskolb, and C. A. Tolman, *Analyt. Chem.*, 1972, **44**, 2010.

The decreasing percentage of [$^2H_0$] at greater times shows the increasing degree of deuteriation expected for stepwise exchange.* A comparison of the percentages of [$^2H_0$]propene and [$^2H_1$]propene obtained from microwave and mass spectroscopy is shown in Table 2. The agreement between the two analytical methods is very good in all cases except for [$^2H_0$]propene in the sample from the second run using the rhodium catalyst. The mass spectral result is less reliable since its determination involved large corrections for mass fragments coming from more highly deuteriated species.

TABLE 2

Percentages of [$^2H_0$]propene and [$^2H_1$]propene from microwave and mass spectrometric analysis

	[$^2H_0$]Propene		[$^2H_1$]Propene	
Catalyst	Microwave [a]	Mass spec.	Microwave	Mass spec.
Pt^{I}	73·7 (0·7)	75	22·6 (0·3)	23
Pt^{II}	63·2 (0·7)	64	29·3 (0·4)	30
Rh^{I}	52·7 (0·7)	55	31·9 (0·5)	32
Rh^{II}	21·3 (1·0)	27	31·6 (1·5)	31
Ni	90·8 (0·8)	89	10·4 (0·1)	10

[a] The quantity in parentheses is one standard deviation.

The distribution of subspecies of [$^2H_1$]propene was determined by microwave spectroscopy (Table 3) and gives information about the mechanism of the exchange. *cis*-CHD=CHCH$_3$ and *trans*-CHD=CHCH$_3$ were produced in a 1 : 1 ratio in all cases and their sum is denoted by 1-E. Subspecies 2-E and 3-E with deuterium exchanged for hydrogen at the second and third carbon atoms of [$^2H_1$]propene were also observed. Inspection of the π-allyl mechanism of exchange shown in equation (2), with R = H, shows that no exchange of the H on C$_2$ of propene for D can occur by this mechanism. The π-allyl mechanism is thus clearly inconsistent with the results of Table 3 which show 2-E in substantial amounts in all cases and as the principal [$^2H_1$] subspecies in the case of Pt. Another feature of the π-allyl mechanism is that 3-E is the only product of the first round of exchange. 1-E Can appear only after two or more exchanges. Thus, (3-E)/(1-E) should be very large early in the exchange and gradually decrease as the reaction proceeds. Though we have not attempted to quench the exchange reactions at very short times to permit extrapolation of (3-E)/(1-E) to $t = 0$, our results strongly suggest that the ratio will not approach infinity at short times and is, in fact, *smaller* at shorter times (Table 3).

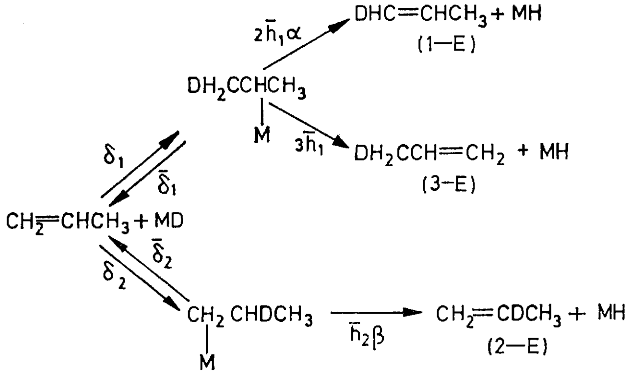
TABLE 3

Distribution (%) of [$^2H_1$]propene subspecies determined by microwave spectroscopy

Species	Pt^{I}	Pt^{II}	Rh^{I}	Rh^{II}	Ni^{I}
$CH_2{=}CDCH_3$	58·0 (0·7) [a]	57·8 (0·6)	30·7 (0·4)	25·4 (0·3)	16·8 (0·4)
$CH_2{=}CHCH_2D$ [b]	26·2 (0·5)	26·6 (0·3)	34·2 (0·4)	40·4 (0·5)	53·1 (0·7)
cis-CHD=CHCH$_3$	7·9 (0·2)	8·0 (0·2)	17·5 (0·3)	17·2 (0·3)	15·3 (0·3)
trans-CHD=CHCH$_3$	8·0 (0·2)	7·7 (0·1)	17·6 (0·3)	17·0 (0·3)	14·8 (0·3)
(2-E)/[(1-E) + (3-E)] [c]	1·38	1·37	0·44	0·34	0·20
(3-E)/(1-E)	1·65	1·69	0·97	1·18	1·76

[a] Estimated uncertainties (one standard deviation) are in parentheses. [b] Data are the sum of *sym* and *asym* $CH_2{=}CHCH_2D$. [c] 1-E, 2-E, and 3-E designate exchanged propene with deuterium in positions 1, 2, or 3. 1-E and 3-E represent sums of species which give distinct microwave spectra, in the latter case, arising from the three rotational positions of the $-CH_2D$ group.

The formation of [$^2H_1$]propenes by the metal hydride addition–elimination mechanism is shown in the Scheme.



SCHEME First stage of H–D exchange on propene by metal hydride addition–elimination mechanism

The upper parth shows Markovnikov and the lower anti-Markovnikov modes of addition. Only the first stage of H–D exchange is shown. The letters δ_1 and $\bar{\delta}_1$ represent the rate constants for making or breaking a bond between deuterium and C$_1$; $\bar{h}_1$ represents the specific rate constant for elimination of hydrogen from the CH$_3$ group of the isopropyl intermediate. The specific rate constants leading to formation of 1-E and 2-E are modified by the factors α and β to account for secondary isotope effects. The secondary isotope effect in the formation of E-3 is expected to be extremely small, and is neglected. Primary isotope effects are included in the δ terms.

By applying the steady state approximation † to the alkyl intermediate, we find in the limit as $t \longrightarrow 0$.

$$(3\text{-E})/(1\text{-E}) = 3/(2\alpha) \tag{3}$$

$$(2\text{-E})/[(1\text{-E}) + (3\text{-E})] = \frac{\delta_2}{\bar{\delta}_1} \times \frac{\dfrac{\bar{h}_2\beta}{\bar{\delta}_2 + \bar{h}_2\beta}}{\dfrac{3\bar{h}_1 + 2\bar{h}_1\alpha}{\bar{\delta}_1 + 3\bar{h}_1 + 2\bar{h}_1\alpha}} = \frac{\delta_2}{\bar{\delta}_1} \times f \tag{4}$$

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* The distribution of deuteriated propenes expected at equilibrium in our experiments with 4·2 × 6 = 25·2 mmol exchangeable H on C_3H_6 and 50 mmol of CH_3OD is *ca.* $(1/3)^6 \times 100 = 0{\cdot}14\%$ [$^2H_0$] and $6(1/3)^5(2/3) \times 100 = 1{\cdot}6\%$ [$^2H_1$].

† A similar mathematical analysis of multiple H–D exchange on propene has been described by Y. Yasuda and K. Hirota, *Z. Phys. Chem.* (*Frankfurt*), 1970, **71**, 81, who, however, assumed no deuterium isotope effects.

The ratio (3-E)/(1-E) permits a determination of the secondary isotope effect α^{-1} and the ratio (2-E)/[(1-E) + (3-E)] is related to the ratio of rates of reactions giving normal or branched alkyls. The data in Table 3 show that the experimental values of (3-E)/(1-E) are close to, but slightly larger than 1·5 for the Pt and Ni catalysts. From these numbers we find $\alpha^{-1} = k_H/k_D = 1{\cdot}10$ in the case of Pt and 1·17 in the case of Ni. With rhodium, the first sample was taken so late in the exchange that the measured ratio may not be indicative of the initial value, and the apparent inverse isotope effect may not be real.

The normal secondary isotope effect observed for Pt and Ni indicates that hydrogen eliminated from the $DH_2CCH(M)CH_3$ intermediates comes preferentially from the CH_3 group. This result can be predicted from a theoretical calculation based on transition-state theory and statistical mechanics.* A similar simplified treatment has been applied by Streitwieser [14] to secondary isotope effects in the solvolysis of deuteriated cyclopentyl tosylates.

One assumes that the ground state for the M–H elimination reaction may be represented by an ordinary isopropyl metal complex while the transition state resembles propene co-ordinated to a transition-metal hydride. Reasonable values for the frequencies of the methylene C–H vibrations, taken from Bellamy [15] and from studies of Zeise's salt, $K[(C_2H_4)PtCl_3]$,[16] are shown in Table 4. Frequencies of the corresponding C–D vibrations are assumed to be reduced by a factor of 1/1·35.[14] This sort of rough estimate gives a value of $\alpha^{-1} = 1{\cdot}18$, in fair agreement with the experimental values. Table 4 shows that the principal contribution to the normal secondary isotope effect is the out-of-plane bending vibration.

TABLE 4

Frequencies (cm^{-1}) of C–H vibrations in ground and transition states for β-elimination from isopropyl intermediate

Vibration	ν_H	$\nu_H^{\ddagger}$	$\Delta\nu$
Stretch	2920	3040	−140
In-plane bend	1450	1425 [a]	+25
Out-of-plane bend	1375	1000	+375
			+235

[a] The b_2 scissoring vibration of $(C_2H_4)PtCl_5^-$ was used because the a_1 scissoring is strongly mixed with the C=C stretch.[16]

The ratio (2-E)/[(1-E) + (3-E)] is determined by two terms as seen in equation (4): the first (δ_2/δ_1) involving the relative rates of anti-Markovnikov and Markovnikov M–D addition and the second (f) involving primary and secondary isotope effects in the β-elimination. Since we cannot determine primary isotope effects directly from our data, f must be estimated in order to arrive at a value for δ_2/δ_1. Fortunately, f is rather insensitive to the isotope effects assumed, ranging in value from 0·71 for $\bar{h}_1/\bar{\delta}_1 = \bar{h}_2/\bar{\delta}_2 = 2$ to 0·91 for a primary isotope effect of 10 (keeping $\alpha = \beta = 0{\cdot}9$). If we assume $f = 0{\cdot}8$ as a reasonable estimate, the ratio of anti-Markovnikov to Markovnikov addition can be estimated by equation (5). The values of δ_2/δ_1 calculated from the

$$\delta_2/\delta_1 \sim \lim_{t \to 0} 1{\cdot}25\,(2\text{-E})/[(1\text{-E}) + (3\text{-E})] \quad (5)$$

data in Table 3 are 1·72 for Pt, 0·55 for Rh, and 0·25 for Ni, corresponding to 63, 35, and 20% anti-Markovnikov addition, respectively.

Comparison of these results with other studies of these same catalysts in the isomerization and H–D exchange of butenes provides some interesting mechanistic insights. The deuteriation/isomerization ratios found for but-1-ene were 1·3 for Pt, 1·0 for Rh, and 0·006 for Ni.[5] Our results suggest that the excess deuteriation in the Pt system is a consequence of preferential anti-Markovnikov Pt–D addition, which leads to deuteriation but not isomerization. In the Rh system we find that the two modes of addition have comparable rates for propene. Cramer [17] finds that Markovnikov addition of the same catalyst to but-1-ene occurs only about once in 15 times. This suggests that the more bulky ethyl group of but-1-ene hinders formation of a secondary alkyl intermediate much more than the methyl group of propene. Cramer has also found that collapse of the s-butyl intermediate formed by Markovnikov addition is *ca.* 9 times as likely to give a but-2-ene as to return to but-1-ene. This indicates a marked preference for β-elimination from the methylene carbon.

The nearly equal rates of deuteriation and isomerization in the rhodium system are a consequence of isomerization of but-1-ene by RhH (probably present as $HRhCl_2S_3$, S = solvent or Cl^-) at a rate comparable to loss of deuterium through exchange which is not accompanied by isomerization. The presence of RhH in a CH_3OD solvent system is a consequence of relatively slow exchange of RhH with solvent compared to the rate of olefin isomerization.

In the nickel system the rate of exchange of solvent deuterium with NiH (in the form of $HNi[P(OEt)_3]_3^+$) is so slow that the nickel hydride produced in the first exchange undergoes about 170 cycles of but-1-ene isomerization before exchanging H for D.[10] This behaviour explains why relatively little deuteriation of propene occurred in 1·5 h at 0 °C while the same catalyst concentration isomerizes but-1-ene to an equilibrium mixture of isomers in a matter of minutes at the same temperature.[10]

The results from the nickel hydride system emphasize the danger of inferring a π-allyl mechanism merely on the basis of a low deuteriation/isomerization ratio. The

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* The interested reader is referred to L. Melander, 'Isotope Effects on Reaction Rates,' Ronald Press Company, New York, 1960 and 'Isotope Effects in Chemical Reactions,' ACS Monograph, C. J. Collins and N. S. Bowman, eds., Van Nostrand Reinhold Company, New York, 1970.

[14] A. Streitwieser, jun., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, 1958, **80**, 2326.

[15] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' John Wiley, New York, 1966, p. 13.

[16] J. Hiraishi, *Spectrochim. Acta*, 1969, **25***A*, 749.

[17] R. Cramer, *Trans. N.Y. Acad. Sci.*, 1971, **33**, 97.

positions of deuterium in deuteriated propenes permit a far more reliable distinction between mechanisms.

Roos and Orchin[18] were led to propose an intramolecular 1,3-hydrogen shift in the isomerization of allylbenzene with $DCo(CO)_4$, since only *ca.* 5% of the product propenylbenzene contained deuterium. Later H–D exchange studies by Taylor and Orchin[19] have conclusively shown that a hydride addition–elimination mechanism was operative. Exchange between $[^2H_6]$-propene and butenes was carried out in the presence of $HCo(CO)_4$. The product mixture was brominated and the dibromopropanes separated by gas chromatography and analyzed by ^1H n.m.r. spectroscopy. Some 20·8% of the monoprotiodibromopropanes were found to contain H on the central carbon. An advantage of our microwave method is that the extent and positions of H–D exchange could have been determined directly by measurements on the propene–butene mixture.

Our results based on analysis of $[^2H_1]$propene are in complete accord with the hydride addition–elimination mechanism for the catalyst systems we have studied, in accord with earlier conclusions of Cramer and Lindsey.[9] It would now be highly desirable to apply propene labelling and microwave spectroscopy to other olefin isomerization systems, such as those involving metal carbonyls,* where π-allyl mechanisms have been proposed † and where a source of metal hydride is not as obvious as in our systems.

We acknowledge helpful discussions on deuterium isotope effects with Professor A. Streitwieser, University of California, Berkeley.

Note added in proof. Dr. Charles P. Casey, of the University of Wisconsin, has recently obtained positive evidence for a π-allyl olefin isomerization mechanism involving iron carbonyl catalysts. We are indebted to Dr. Casey for a copy of his paper prior to its publication.

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* This could be readily done by exposing a mixture of C_3H_6 and C_3D_6 to the isomerization catalyst, then analysing the products by microwave for $[^2H_1]$products.

† π-Allyl mechanisms of olefin isomerization by $Fe(CO)_5$ have been suggested by T. A. Manuel, *J. Org. Chem.*, 1962, **27**, 3941 and G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, 1962, **84**, 4591.

[18] L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, 1965, **87**, 5502.

[19] P. Taylor and M. Orchin, *J. Amer. Chem. Soc.*, 1971, **93**, 6504.