*The Isotopic Hydrogen Exchange between Propene and Deuterium Oxide Catalyzed by Nickel Powder**

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The catalyzed, isotopic hydrogen exchange of olefins and related compounds with hydrogen gas has been investigated by many workers for thirty years[1] in connection with the mechanism for the catalytic hydrogenation of double bonds.[2] Similar exchange reactions with water have not been reported so much, though it is simpler to clarify their mechanisms because of the lack of simultaneous hydrogenation. One of us (K. H.) studied the exchange reaction of paraxylene with deuterium oxide and found that only the exchange of methyl hydrogen could be recognized at 100°C in the presence of nickel powder.[3] Similar characteristic catalytic activity was recently reported by Crawford and Kemball[4] on nickel films in the exchange of alkylbenzenes; however, they used deuterium gas instead of deuterium oxide.

On the other hand, rhodium, palladium and

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* Preliminary reports: "Shokubai" (Tokyo), **4**, 41, 371 (1962).

[1] A. Farkas and L. Farkas, *Nature*, **132**, 894 (1933); J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[2] Cf. D. D. Eley, "Catalysis" (Ed. by P. H. Emmett), **3**, 49 (1955); T. I. Taylor, ibid., **5**, 257 (1957).

[3] K. Hirota, T. Ueda, et al., a) *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 362 (1960); b) This Bulletin, **33**, 423 (1960); c) **35**, 228 (1962).

[4] E. Crawford and C. Kemball, *Trans. Faraday Soc.*, **58**, 2452 (1962).

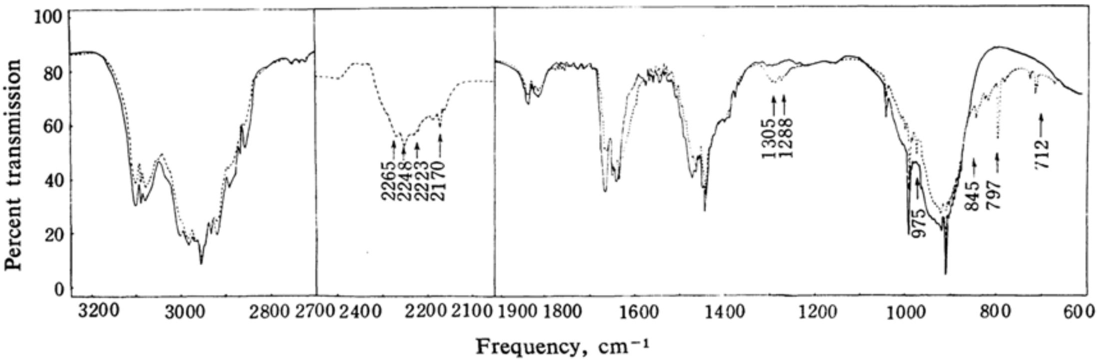

Fig. 1a. IR spectra of propene and the product of deuterium exchange (No. A-4).

—— Propene ---- Reaction product on Ni

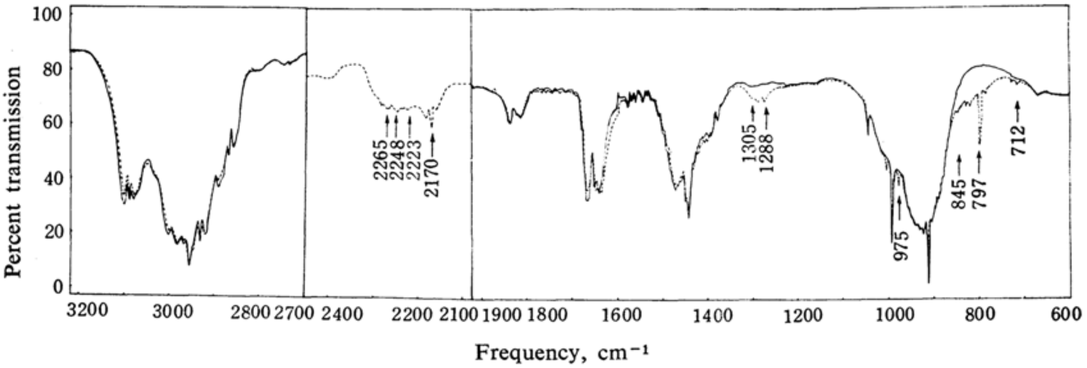

Fig. 1b. IR spectra of propene and the product of the deuterium exchange (No A-9).

—— Propene ---- Reaction product on Ni-Al_2O_3

platinum—the metals also with a face-centered cubic lattice—were found to exchange ring hydrogen to the same order of magnitude under the same experimental conditions.[3c]

Such difference in reaction would seem of interest in order to understand the nature of selectivity on catalytic hydrogenation, so the study has been extended to other olefinic compounds with methyl groups. The exchange reaction of propene with deuterium oxide by the use of nickel catalysts, supported and unsupported, will be described in the present report.

Experimental

Materials. — Commercial pure isopropanol was dehydrated with activated alumina. The propene thus obtained was purified by distillation in vacuo. The deuterium oxide (99.7%) obtained from Showa Denko K. K. was used without any further purification. The other materials were commercial grade pure reagents.

The nickel catalyst was prepared by decomposing commercial nickel formate (Mitsuwa Yakuhin Kogyo K. K.) at 270°C and then degassing it at the same temperature for about 20 hr. A nickel catalyst supported on alumina in the ratio 1 : 1 was prepared by the thermal decomposition of nickel formate supported on activated gamma-alumina (Wako Junyaku K. K.). The nickel formate was prepared as follows:—Nickel carbonate was obtained by the addition of ammonium carbonate into a nickel nitrate solution; the precipitate was washed until the filtrate did not show any alkaline reaction. The dried nickel carbonate and activated alumina (Al_2O_3 : Ni = 1 : 1 in weight) were mixed well, and then water was added to the mixture until it became a a jelly substance. This jellified mixture was turned into nickel formate by treating it with formic acid. In order to precipitate the formate on alumina completely, acetone was added finally; then the precipitate was dried for 24 hr. at 80°C.

Procedure.—The reaction was always carried out in a glass ampoule into which propene and deuterium oxide had been charged in vacuo. The detailed procedure was nearly the same as that already reported by one of the present authors.[3]

For the quantitative analysis of the deuterated products, both mass-spectrometry (Hitachi RMU-5 installed at the Osaka Laboratory, Japanese Association for Radiation Research on Polymers) and NMR spectrometry (Varian A-60) were adopted.

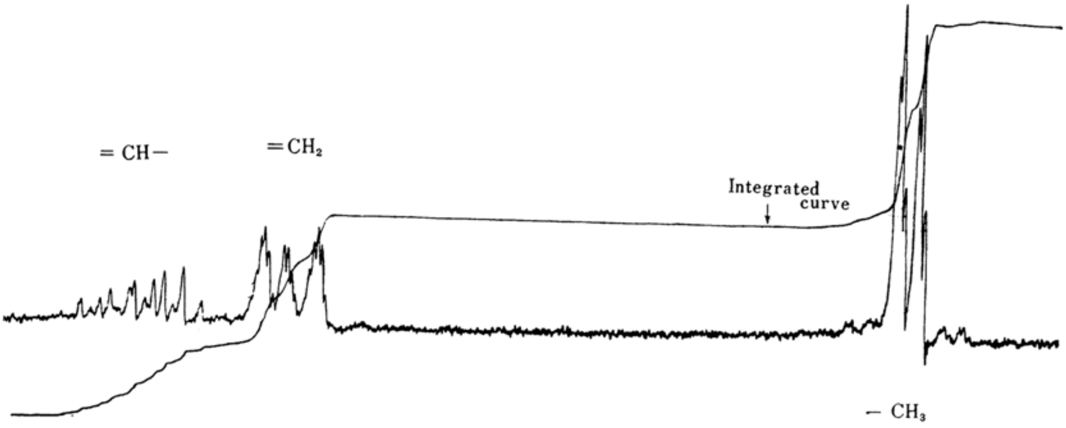

Fig. 2a. NMR spectrum of propene.

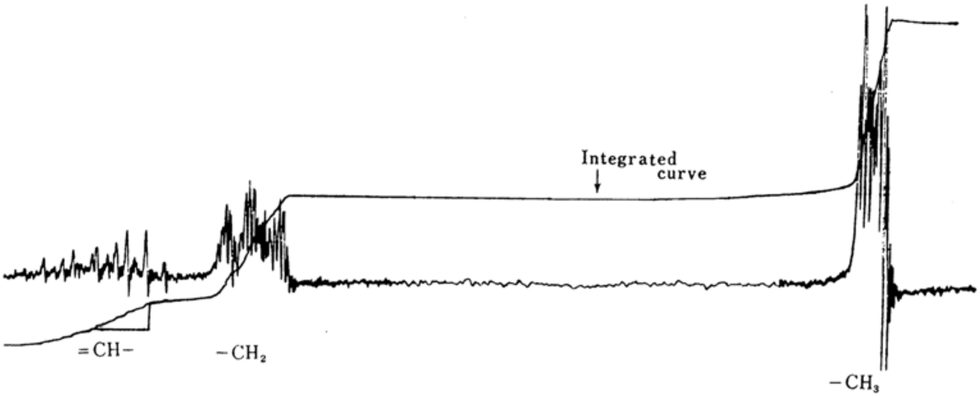

Fig. 2b. NMR spectrum of No. A-4.

For the qualitative analysis, however, infrared-spectrometry (Hitachi EPI-2 and DS 402G of Japan Spectroscopy Co.) was adopted.

Results

Deuterium Distribution.—Table I shows the deuterium distribution in the products which were produced under the experimental conditions described, with $C_3H_{6-i}D_i$ denoted by d_i. Generally speaking, propene exchanged more easily than *p*-xylene with D_2O, because the reaction is measurable even at room temperature.* Secondly, the data on nickel seem to show that the exchange proceeded as a successive reaction, judging from the deuterium distribution in the products. The Datum of No. K1-*i* is a part of those of No. K1 shown in Table II, which gives another indication of the successive production of d_2 via d_1, because the d_1% vs. time curve reaches a maximum value at 5 hr.

The Identification of the Deuterated Groups.—Before entering into a detailed discussion, let us investigate the deuterated groups in the products on No. A4, which was obtained without any carrier, by comparing the infrared spectra (dotted line in Fig. 1a) with that of propene (solid line in Fig. 1a). The infrared data of deuteropropenes obtained by various researchers[5-8] seem to show that the deuterium exchange occurs more easily at the vinyl group rather than at the methyl group in the 2100～2300 cm^{-1} region; because the C–D stretching bands of the vinyl group appearing at 2248 and 2265 cm^{-1} in Fig. 1a show stronger intensities than the bands of $-CH_2D$ appearing at 2161, 2170 and 2183 cm^{-1}[8]

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* However, so far as the exchange of methyl hydrogen is concerned, the rates may not be so different, as will be found.

5) B. S. Rabinovitch and F. S. Looney, *J. Am. Chem. Soc.*, **75**, 2652 (1953) and a private communication.

6) a) R. C. Lord and P. Venkateswarlu, *J. Opt. Soc. Am.*, **43**, 1079 (1953); b) M. Farina and M. Peraldo, *Gazz. Chim. Ital.*, **90**, 973 (1960).

7) G. Zerbi, M. Peraldo and E. Mantica, Symposium of Molecular Structure and Spectroscopy, Tokyo, C 213 (1962).

8) Private Communication from Murahashi Lab. of Osaka University.

TABLE I. DEUTERIUM DISTRIBUTION IN THE PRODUCTS

No.	Catalyst, g.		Sample, mol. ×10³		Reaction temp., °C	Time hr.	Products, %					
			C_3H_6	D_2O			d_0	d_1	d_2	d_3	d_4	d_5
A4	Ni	5	6.96	21.7	11.5	ca. 240	42.$_5$	40.$_6$	13.$_3$	2.$_1$	—	—
A5	Ni	5	7.58	21.5	38.1	17	57.$_8$	32.$_4$	6.$_9$	2.$_9$	—	—
K1-i*	Ni	5	4.14	15.8	38.1	44.0	6.$_5$	19.$_1$	29.$_4$	27.$_0$	14.$_6$	3.$_4$
A6	Ni-Al_2O_3	3.7	7.32	23.6	38.1	44	72.$_2$	23.$_9$	4.$_9$	—	—	—
A7	Ni-Kieselguhr	10	5.95	51.5	38.1	107	23.$_8$	38.$_1$	28.$_6$	9.$_5$	—	—
A8	Ni-Kieselguhr	10	5.95	16.3	38.1	48	47.$_6$	35.$_2$	17.$_6$	—	—	—
A9	Ni-Al_2O_3	5	6.00	18.1	18.6	354	63.$_6$	29.$_8$	5.$_9$	—	—	—
B19-a	Ni	1.65	2.18	10.7	25.0	25	51.$_6$	36.$_8$	10.$_1$	1.$_5$	—	—
B19-b	Ni	1.65	2.18	11.0	25.0	50	39.$_7$	40.$_5$	15.$_5$	3.$_6$	0.$_7$	—
B19-c	Ni	1.65	2.18	10.7	25.0	100	26.$_8$	40.$_1$	23.$_8$	7.$_8$	1.$_5$	—

* The progress of the change of deuterium distributions in K1 is shown in Table II.

TABLE II. KINETICS OF ISOTOPIC HYDROGEN EXCHANGE BETWEEN D_2O AND C_3H_6 ON Ni CATALYST (No. K-1)

	Reaction time min.	Percent distribution of deuterated propenes						$\phi = \sum i d_i$	k_ϕ min^{-1}	k_0 min^{-1}
		d_0	d_1	d_2	d_3	d_4	d_5			
a	0	97.$_0$	3.$_0$	—	—	—	—	3.$_0$		
b	34	90.$_1$	8.$_8$	1.$_1$	—	—	—	11.$_0$	0.32$_9$	0.21$_0$
c	72	84.$_1$	13.$_8$	2.$_1$	—	—	—	18.$_0$	0.25$_7$	0.19$_2$
d	126	75.$_1$	22.$_8$	2.$_1$	—	—	—	27.$_0$	0.22$_3$	0.19$_6$
e	180	65.$_5$	28.$_6$	4.$_7$	1.$_2$	—	—	41.$_6$	0.24$_6$	0.21$_1$
f	240	60.$_6$	31.$_2$	6.$_6$	1.$_6$	—	—	49.$_2$	0.22$_1$	0.19$_0$
g	300	50.$_5$	37.$_4$	10.$_3$	1.$_8$	—	—	63.$_4$	0.23$_4$	0.21$_0$
h	1076	13.$_9$	28.$_7$	30.$_3$	18.$_9$	6.$_6$	1.$_6$	180.$_4$	0.24$_1$	0.17$_6$
i	2624	6.$_5$	19.$_1$	29.$_4$	27.$_0$	14.$_6$	3.$_4$	234.$_3$	0.15$_3$	0.09$_8$

Table III. Assignment of the IR bands of the products

Normal propene				No. 4A			
Frequency cm^{-1}	Intensity		Assignment	Frequency cm^{-1}	Intensity		Assignment
3100	s	R	CH_2 stretching	3100	*		
3090	s	Q		3090	*		
3080	s	P		3080	*		
3000	s	R	CH_2 stretching (sym.)	3000	*		
2990	s	Q		2990	*		
2984	vs	P		2984	*		
2967	s	R	CH_3 stretching (anti.)	2967	*		
2955	s	Q		2955	*		
2948	s	R	CH_3 stretching (anti.)	2948	*		
2933	s	Q		2933	*		
2920	s	P		2920	*		
2890	m	R	CH_3 stretching (anti.)	2890	*		
2870	m	Q		2870	*		
2858	w	P		2858	*		
				2294	w		
				2281	w		
				2265	w		*t*-1-d_1
				2248	w		*c*-1-d_1, 2-d_1
				2223	w		1,1-d_2(3-d_2)
				2183	w	(R)	3-d_1
				2170	w	(Q)	
				2161	w	(P)	
1838	w	R	CH_2 bending ($2\times\nu_{912}$)	1838	*		
1824	w	Q		1824	*		
1815	w	P		1815	*		
1665	s	R	C=C stretching	1665	*		
1650	m	Q					
				1645	m		*t*-1-d_1, 2-d_1
1640	s	P					
				1634	m		*t*-1-d_1
				1628	m		*c*-1-d_1, 1,1-d_2
				1613	m		1,1-d_2, 2-d_1
1472	m			1472	**		
1465	m		CH_3 bending (anti.)	1465	**		
1460	s			1460	**		
1448	m	R	CH_3 bending (anti.)	1448	**		
1443	s	Q		1443	*		
1400	m	R	CH_3 bending (sym.)	1400	*		
1375		Q		1375	*		
				1305	vw		3-d_x
				1288	vw		3-d_x
1043	w	Q	CH_3 bending	1043	*vw		
				1000	vw		
990	s	Q	CH bending	990	*		
985	vw	Q	CH bending	985	*		
				975	vw		*t*-1-d_1
963	vw		?	963	*		
918	w	Q	C–C stretching	918	*		
912	vs	Q	CH_2 bending	912	*		
				845	w		2-d_1
				830	w		3-d_1
				823	w		*t*-1-d_1
				815	w		
				797	m		c-1-d_1
				782	w		
				728	vw		1,1-d_2
				712	w		1,1-d_2

* The intensity decreased.

** Shapes of the bands changed and their intensities decreased.

in the products. This finding is interesting if compared with the fact that the exchange occurred overwhelmingly at the methyl hydrogen in the case of *p*-xylene.*

In order to confirm such an unexpected result, the NMR spectrum of the products of No. A4 was measured in the liquid state. As Fig. 2 shows, the above tendency was also observed. The signal of the methyl protons was complicated by the pertial deuteration of both

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* The exchange degree at the ring hydrogen was estimated to be less than 5%, if it occurred at all.[3a)]

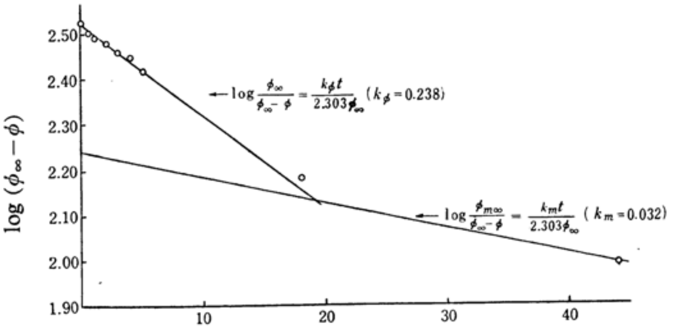
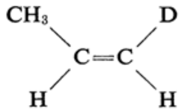


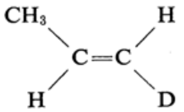
Fig. 3. Plots of log $(\phi_\infty - \phi)$ vs. time.

hydrogens of the methin and methen groups.

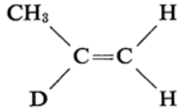
To summarize the above conclusion, all the bands of No. A4 can be assigned as shown in Table III, where the nomenclature used for deutero-propenes deuterated at the vinyl groups is as follows:



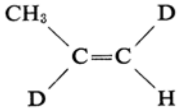
cis-propene-1-d_1
(c-1-d_1)



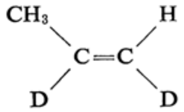
trans-propene-1-d_1
(t-1-d_1)



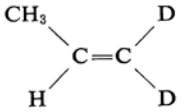
propene-2-d_1
(2-d_1)



trans-propene-1,2-d_2
(t-1,2-d_2)



cis-propene-1,2-d_2
(c-1,2-d_2)



propene-1,1-d_2
(1,1-d_2)

Table III shows further that the bands of medium intensity at 1613, 1628, 1643 and 1645 cm^{-1}, as well as other bands at shorter wavelengths, support the above conclusion. However, even if the exchange at both hydrogens of the methin and methen groups is found, the exchange degree is hard to determine quantitatively on the basis of the infrared data alone. According to the NMR measurement which is now in progress, the exchange at the methin hydrogen appears to be easier.

Kinetics of the Reactions. — In order to investigate the progress of the exchange reaction, the kinetic data of No. K1 (Table II) were analyzed by plotting log $(\phi_\infty - \phi)$ against t. As curve a in Fig. 3 indicates, a straight line was obtained at the initial stage, suggesting that the reaction is of the first order, when only d_1, d_2 and d_3 were the products. This result is concordant with the fact that the exchange proceeds mostly at the hydrogen atoms of the reactive vinyl hydrogen. The failure of linearity at the later stage, when propene-d_4 was produced, may, however, be ascribed to the fact that the less reactive methyl hydrogen began to play the main role in the exchange as the exchange equilibrium of the vinyl hydrogen was gradually attained. Therefore, by the method given by Kemball and Crawford,[4] the ratio of the rate constant of methyl hydrogen, k_m, to that of vinyl hydrogen, k_v, was calculated, assuming the initial rate constant to be 0.23_8. The solid line in Fig. 3 was drawn by using the k_v/k_m $=6.4$ thus obtained.

The explanation assuming the reactivity of different hydrogens can be justified by the deuterated products of Nos. B19-a, -b and -c (Table I), in which the long reaction times of 25, 50 and 100 hr. respectively at 25°C were adopted. In this series, the curve plotting log d_0 vs. time is not linear, as in the case of No. K-1 (cf. Fig. 2), suggesting the presence of at least two kinds of hydrogen atoms with different reactivities. Besides, as Fig. 4 shows, the infrared spectra of Nos. 19 indicate the successive production of propenes deuterated at both the vinyl (2265 and 2248 cm^{-1}) and methyl (2183 cm^{-1}) groups with time, and shows parallel with the increase of propene-d_2 (cf. the bands at 2223 cm^{-1} as well as at 712 cm^{-1} which are not shown). The ratio of d(methyl)/d(vinyl) was preliminarily estimated on the basis of the infrared bands in Fig. 4 to be 3, if the amount of propene-d_1 is proportional to the absorbance of the bands at 2248 cm^{-1} and 2265 cm^{-1} for vinyl and at 2183 cm^{-1} for methyl C–D stretching respectively, and if their absorption coefficients are equal. The numerical value 3 above mentioned coincides with that of 3.4 determined by the

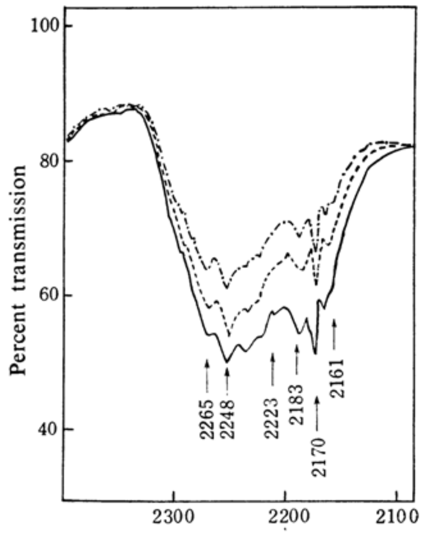


Fig. 4. IR spectra of Nos. B19-a, B19-b and B19-c.

—·— B19-a ---- B19-b —— B19-c

NMR data,* within the range of experimental error.

Effect of Carriers. — As has already been reported,[3] both methyl and ring hydrogen of *p*-xylene were exchangeable if nickel was supported on alumina.[3] Some change in selectivity was also found in the present reaction by the comparison of infrared data of Nos. A5, 6, 7, 8 and 9 with each other, although the change occurred in the direction opposite to that of paraxylene. For example, in the spectrum of No. A-9 shown in Fig. 1b, the band at 2183 cm^{-1} is stronger than those at 2248 and 2265 cm^{-1}. Thus the exchange rate of methyl hydrogen became comparable with or larger than that of vinyl hydrogen as a result of the use of this carrier.

Another point to be mentioned is the absolute decrease in the catalytic activity of carried catalysts. As Table I shows, the exchange degree of Nos. A6, A7, A8 and A9 became similar to that of No. A5 when the reaction time or the amount of the catalyst was increased, while in the case of paraxylene, the activity was always increased by the use of carriers.

Discussion

Propene was found to exchange its three kinds of hydrogen with deuterium oxide. Such a simultaneous exchange of different kinds of hydrogen has already been reported by Twigg[9] on the system when propene and deuterium gas came in contact with the nickel catalyst. Since his results were obtained indirectly by the determination of the total isotopic concentration, it may be said that his conclusion was first confirmed without ambiguity by the present report. It has been found, moreover, that the exchange of methyl hydrogen is more difficult than that of vinyl hydrogen. This finding is to be explained as follows.

As has already been mentioned, the scission of the methyl hydrogen of paraxylene is easier than that of ring hydrogen from the thermochemical viewpoint, because $D(C_6H_5CH_2\text{–}H)$ is 77.5 kcal./mol. and $D(C_6H_5\text{–}H)$ is 104 kcal./mol., according to Szwarc's data.[10] These numerals are favorable for use in the explanation of the experimental results of the exchange reaction carried out on a nickel catalyst. However, the same argument cannot be applied in the present case. Since $D(CH_2:CH\cdot CH_2\text{–}H)$ is 76.5 kcal./mol. and $D(CH_2CH\text{–}H)$ is 104 kcal./mol., the scission of vinyl hydrogen would be more difficult than that of methyl hydrogen, unlike the present exchange data. The above contradiction may not be very serious, however, because no attention was paid in the argument to the existence of a catalyst on which olefins may be adsorbed at their double bond. Moreover, it must be remembered that the two absolute rates of the exchange of methyl hydrogen are not so different as those which occur in the double bonds.

On the exchange reaction of ethene and heavy water, ethene is often regarded, since Horiuti-Polanyi's work,[1] as forming bonds with metals opening its double bond as follows:

$$C_2H_4 \rightarrow H_2\underset{*}{C}\text{–}\underset{*}{C}H_2 \rightarrow H_2\underset{*}{C}\text{–}CH_3$$

where the star $*$ denotes the bonding thereby produced. From such an adsorbed state of the associated type, a half-hydrogenated state, $\underset{*}{C}H_2\text{–}CH_3$, is produced if a sufficient amount of $\underset{*}{H}$ exists on the surface. These presumed species were recently concluded to be present in ethene and higher olefins by the application of the infrared method[11] so far as silica-supported nickel was concerned. It is natural to adopt the same line of argument in the present exchange reaction, assuming the following scheme:

$$\underset{\text{(I)}}{CH_3\text{–}C_2H_3} \rightarrow \underset{\text{(II)}}{CH_3\text{–}\underset{*}{C}H\text{–}\underset{*}{C}H_2} + \underset{*}{D}$$

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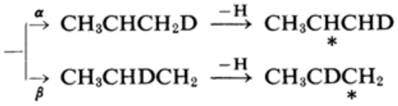
* Details will be published in the future.

[9] G. H. Twigg, *Trans. Faraday Soc.*, **35**, 934 (1939).

[10] M. Szwarc et al., *Proc. Roy. Soc.*, **A207**, 5 (1951).

[11] W. A. Pliskin and P. P. Eischens, *J. Chem. Phys.*, **24**, 482 (1956).



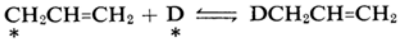
$$-\begin{cases}\xrightarrow{\alpha} \mathrm{CH_3CHCH_2D} \xrightarrow{-H} \mathrm{CH_3CH\underset{*}{C}HD}\\ \xrightarrow[\beta]{} \mathrm{CH_3CHDCH_2} \xrightarrow{-H} \mathrm{CH_3CD\underset{*}{C}H_2}\end{cases}$$

(III)

However, propanes would not be produced due to the low surface concentration of $\underset{*}{\mathrm{D}}$ in equilibrium with D_2O. The degree of deuterium substitution at the methin or methen group in propene-d_1 may be determined by the relative rate of steps α and β.

The assumption of the adsorbed state II, according to which the most stable valency angle, θ, of carbons would be near to the tetrahedral valency angle of 109°28′, may be allowed for geometrical reasons, as has been shown by Twigg and Rideal.[12] Using recent data,* the angle θ is estimated to be 105° if the distance of closest packing is assumed to be 2.47Å, instead of the lattice constant of nickel. This angle is an allowable magnitude for propene to be chemisorbed. On the other hand, the intermediate II, if produced, may not be so stable in the case of paraxylene because of the break in the resonating benzenoid structure. This is the reason why the exchange rate of the ring hydrogen was so small as not to be measured at 100°C in the presence of nickel, while it could be measured in the presence of platinum the angle θ of which was calculated to be 108°17′.

Besides the above adsorbed state, some other state must be assumed to explain the exchangeability of methyl hydrogen. Considering the magnitude of bond-energy mentioned above, an intermediate with the structure of $\underset{*}{\mathrm{CH_2}}$–CH=CH$_2$ may be produced easily on nickel. The deuterium exchange would proceed by the interconversion of species IV and V:

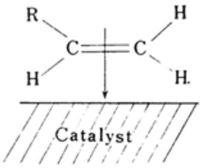


$$\underset{*}{\mathrm{CH_2}}\mathrm{CH{=}CH_2} + \underset{*}{\mathrm{D}} \rightleftharpoons \mathrm{DCH_2CH{=}CH_2}$$

(IV) (V)

where $\underset{*}{\mathrm{CH_2}}\mathrm{CH{=}CH_2}$ may be expressed by $\dot{\mathrm{C}}\mathrm{H_2}$–CH=CH$_2$, considering the stability of this allyl radical. However, there remains a possibility that the adsorbed species IV may be formed by the isomerization of II. By this process the exchange may occur.*

It must be added that a π-complex intermediate may be formed as an adsorbed state, VI, of ethane and its derivatives, as has been proposed by Crawford and Kemball in the exchange of xylenes with deuterium[4] as well as in some heterogeneous catalyses generally. However, in order to make the exchange proceed, an assumption that the state III is in equilibrium with the state VI is necessary. For sake of simplicity, the traditional state II, allowable from the energetic viewpoint, was adopted in the above discussion.



(VI)

There remains one point to be discussed, i. e., whether the intermediates II—IV mentioned above are charged or not, through they have been treated as if uncharged. This problem will be discussed in a future report.

Summary

Deuterium exchange between propene and deuterium oxide has been found to occur at room temperature successively on a nickel catalyst, but about six times more easily at the vinyl hydrogen than at the methyl hydrogen at room temperature, although this finding is not concordant with the expectation derived from the scission energy of the bonds concerned and although it is also different from the easier exchangeability of the methyl hydrogen in the similar exchange reaction of paraxylene.

The discrepancy has been explained by assuming the classical chemisorbed species of propene as an intermediate, i. e., a state of propene which forms bonds between nickel atoms and the C=C group, besides the formation of adsorbed allyl type species on nickel.

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[12] G. H. Twigg and E. K. Rideal, *Trans. Faraday Soc.*, 36, 533 (1940).

* C-C 1.53Å, C-Ni 1.82Å, and Ni-Ni 2.47Å (cf. L. Pauling, "Nature of the Chemical Bonds," 2nd ed. (1962)).

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