Metal-Catalyzed Hydrogenation and Exchange of Cyclohexene[1a]

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Received March 2, 1966

During deuterogenation over 5% palladium-on-charcoal, 5% platinum-on-charcoal, and reduced platinum oxide catalysts cyclohexene desorbs with deuterium in either its allylic or olefinic position. Because this is not accommodated by the classical mechanism, a new surface species is postulated which involves an intramolecular hydrogen shift.

Various evidence suggests nonclassical surface intermediates in hydrogenation and exchange reactions of hydrocarbons over metal catalysts.[2] We wish to contribute new evidence which is unexpected from classical intermediates, but understandable by modified nonclassical ideas.

During the hydrogenation of cycloalkenes with deuterium, exchanged olefins desorb from the surface. Predictions of the classical mechanism[3] are shown in Figure 1.

Paths I–V produce olefin exchanged in allylic but not in olefinic positions. Only desorption followed by readsorption on the opposite face of the ring (V–IX) can lead to deuterium on the double bond and this necessarily puts deuterium in the allylic position, IX. If deuterium attacked the other surface bond in VI, *trans*-3,4-dideuteriocyclohexene could desorb, and, of course, other exchanged species may arise by further migration of bonds and attack of deuterium or hydrogen.

We have recently shown the absence of double-bond migration during the hydrogenation of (+)-1-*p*-menthene over platinum.[4] Other evidence suggests massive double-bond migration during the hydrogenation of 1,2-dimethylcyclohexene over platinum.[5,6] Because the methyl groups in these two compounds may influence the type of species formed on the surface, it is of interest to investigate the behavior of unsubstituted cycloalkenes. In a previous paper we reported on the *cis*- and *trans*-cyclodecene system[7] and here we report on the exchange of cyclohexane.

Experimental Section

Neat cyclohexene was partially hydrogenated with deuterium (General Dynamics, 99.5%) at 1 atm and room temperatures (28–31°) in an apparatus similar to one previously described.[5] Three different catalysts were used, PtO_2 (Goldsmith Brothers, Chicago, Ill.), 5% platinum–charcoal, and 5% palladium–charcoal (Engelhard). Following reduction the reaction mixtures were filtered and analyzed by gas–liquid partition chromatography (glpc) and nuclear magnetic resonance spectroscopy (nmr). The glpc equipment was an Aerograph A90-P (Wilkens Instrument Corp.) equipped with a 73 ft × 0.25 in. L.A.C. column at 140°; per cent compositions were calculated by the method previously described.[5] The nmr equipment consisted of an A-60 console and DP-60 power supply and magnet (Varian Associates). Spectra and integrals of reaction mixtures were obtained along with similar data for light cyclohexene–cyclohexane standards. The same nmr sample tube was used for light and deuterated mixtures of about the same composition. Olefinic and allylic proton areas were divided by one-fourth of the area due to the protons in the 4 and 5 positions. Decreases in areas were attributed to the presence of deuterium. Mass spectra were obtained by Mr. J. Neuzil of the Institute of Gas Technology and calculations were made as previously described by hand[8] and also by computer with a program written by Mr. B. Rosen.

Results

Results from nmr measurements of the filtered reaction mixtures are shown in Table I; the major source of error seems to be in measuring the integrals. For cyclohexene–cyclohexane mixtures this presents some problem because of small overlap between the hydrogens at the allylic and the 4 and 5 positions and between the latter and the cyclohexane hydrogens. However, this can be done with fair accuracy as demonstrated in Table II for several standard mixtures. Accuracy at the olefinic position is highest because this set of peaks is far downfield from the rest. We estimate the maximum error in olefinic positions to be ±0.09 and in allylic to be ±0.15; the respective average deviations are ±0.05 and ±0.08.

TABLE I

LIQUID CYCLOHEXENE EXCHANGED WITH DEUTERIUM OVER THREE CATALYSTS

Expt no.	Catalyst, g	Cyclohexane, %	Relative no. of hydrogens and deuteriums in exchanged cyclohexene: Olefinic		Allylic	
			H	D[a]	H	D[b]
20	Pt–C, 0.011	7.8	1.94	0.06	3.96	0.04
17A	Pt–C, 0.0097	11.0	1.93	0.07	3.94	0.06
18	Pt–C, 0.0191	15.8	1.91	0.09	3.89	0.11
17B	Pt–C, 0.0095	20.9	1.84	0.16	3.84	0.16
19	Pt–C, 0.0297	24.5	1.75	0.25	3.58	0.42
21	Pt–C, 0.0141	43.8	1.77	0.23	3.67	0.33
			1.74	0.26	3.73	0.27[c]
22	Pt–C, 0.0018	83.5	1.45	0.55	3.26	0.74
26	PtO_2, 0.0041	5.3	1.88	0.12	3.83	0.16
24	PtO_2, 0.0048	26.3	1.76	0.24	3.61	0.39
27	PtO_2, 0.0037	44.9	1.63	0.37	3.63	0.37
28	PtO_2, 0.0032	63.3	1.53	0.47	3.57	0.43
29	Pd–C, 0.0120	20.6	1.84	0.16	3.75	0.25
30	Pd–C, 0.0083	49.7	1.71	0.29	3.64	0.36
31	Pd–C, 0.0081	70.0	1.49	0.51	3.34	0.66
			1.39	0.61	3.29	0.71[c]

[a] Number of H's subtracted from 2.00. [b] Number of H's subtracted from 4.00. [c] Separate analysis.

That these error limits may be low is suggested by the average deuterium contents obtained from mass

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(1) (a) Presented in part before the Organic Division at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964. (b) To whom inquiries concerning this work should be sent: Department of Chemistry, Southern Illinois University, Carbondale, Ill. 62901

(2) (a) F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catalysis*, **1**, 255 (1962); (b) J. J. Rooney and G. Webb, *ibid.*, **3**, 488 (1964).

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(7) G. V. Smith, *ibid.*, **5**, 152 (1966).

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TABLE II

NMR ANALYSES OF STANDARD MIXTURES

Cyclohexane, %	No. of H's in cyclohexene[a] Olefinic	No. of H's in cyclohexene[a] Allylic
4.4	1.99	3.98
8.5	1.97	3.93
	1.98[b]	3.94[b]
20.1	2.09	4.15
39.4	2.04	4.11
	2.09[b]	4.14[b]
46.7	2.04	4.06
58.8	2.04	4.07

[a] Compared to four H's in positions 4 and 5. [b] Repeat analysis.

spectral data, Table III. Both compounds show less deuterium by mass spectral analysis than by nmr. This probably arises from the assumption that the nmr peaks overlap to the same extent in the reaction mixtures as they do in the standard mixtures. It was assumed that separation of the integrals of the experimental mixtures should match separation of the integrals of the standard mixtures; line broadening due to deuterium in the experimental mixtures may lower this accuracy. The dearth of species beyond d_2 indicates that little deuterium exists in the 4 and 5 positions, a conclusion supported by the fact that double-bond migration is slow on platinum.[8]

TABLE III

MASS SPECTRAL RESULTS FOR EXCHANGED CYCLOHEXENES

D[a]	Expt 21, Pt-C	Expt 27, PtO_2
d_0	78.90[b]	75.07[b]
d_1	15.85	17.24
d_2	3.70	4.87
d_3	1.02	1.60
d_4	0.34	0.65
d_5	0.11	0.28
d_6	0.042	0.14
d_7	0.019	0.081
d_8	0.0083	0.034
d_9	0.0034	0.017
d_{10}	0.0011	0.0053
Av D[c]	0.287	0.377

[a] Species containing no deuteriums, d_0; one deuterium, d_1; two deuteriums, d_2; etc. [b] Percentages. [c] Average number of deuteriums per molecule.

Experiments were carried out to determine the extent, if any, of rate limiting by deuterium diffusion through the liquid.[9] The apparatus was crude for this but the rate data obtained are shown in Table IV.

TABLE IV

RATE VARIATIONS WITH CATALYST WEIGHT

Expt	Catalyst, g	Temp, °C	Rate, cc of H_2/min/g of cat
	Pt-C		
17	0.0096	25.0	223
18	0.0191	28.0	256
19	0.0297	29.0	258
	PtO_2		
24	0.0048	32.5	1028
25	0.0087	33.0	767
23	0.0171	30.5	643
	Pd-C		
29	0.0120	32.0	635

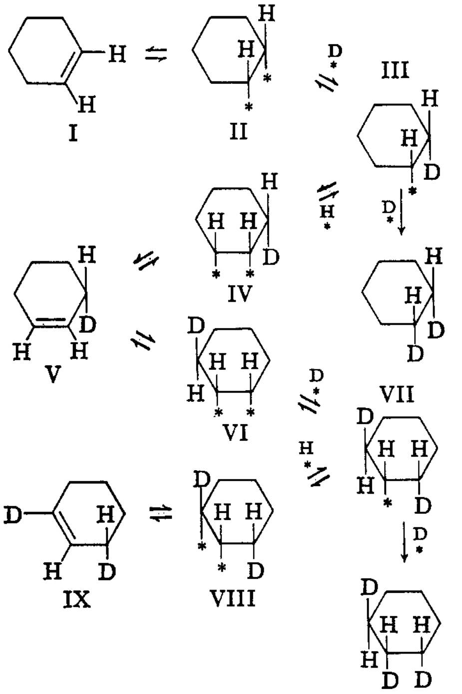


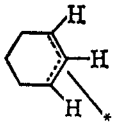
Figure 1.—Classical mechanism for exchange and reduction of cyclohexene on metal surfaces. Asterisks represent surface sites.

Tripling the catalyst weight for platinum on charcoal has little effect on the rate per gram of catalyst; however, increasing the weight of platinum oxide results in a decreased rate per gram of catalyst and indicates diffusion limitation. Diffusion control probably occurred over Pd–C as suggested by the relatively fast rate in expt 29. No noticeable effects on deuterium distributions can be correlated with diffusion control.

Discussion

Olefinic and allylic hydrogens are exchanged for deuterium over all three catalysts and the extent of exchange is approximately the same in both positions (Figure 2). These facts could be rationalized by Figure 1 if it were not for the mass spectra revealing at least 70% of the exchanged cyclohexenes to be monodeuterio (Table III). Since addition is approximately twice as fast as olefin exchange (Table III, 20–25% exchanged cyclohexene at 44% cyclohexane), the surface deuterium concentration must be high and yield little light cyclohexene upon exchange; *i.e.*, the addition reaction lowers the surface concentration of hydrogen produced during cyclohexene exchange. A similar situation occurs with 1-hexene and 1,9-octalin.[8]

These facts cannot be explained by any process involving only mono- and diadsorbed species as shown in Figure 1 and other possibilities must be considered. A π-allyl species (X) has been proposed for exchange of certain saturated hydrocarbons.[10] Exchange is postu-



X

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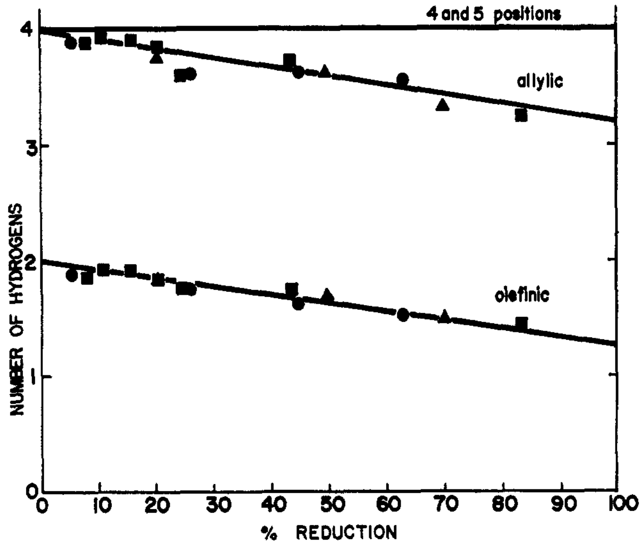


Figure 2.—Amounts of deuterium present in recovered cyclohexene at various percentages of reduction: ▲, 5% Pd–C; ■, 5% Pt–C; and ●, PtO_2.

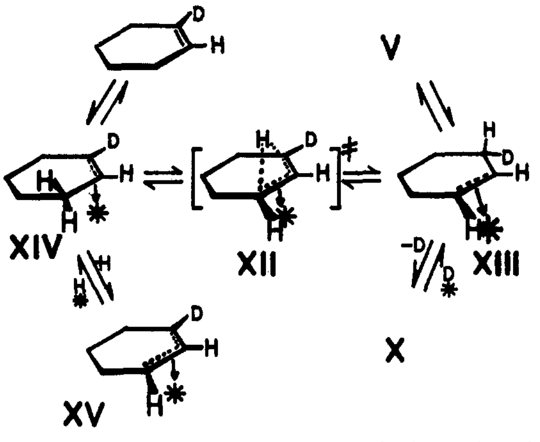
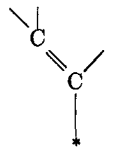


Figure 3.—Various structures related to the formation of XII. The difference between XIII and IV is not clear; they may be the same species. Asterisks represent surface sites.

lated by attack of deuterium to either the top of bottom of the carbons at the ends of the allyl system, but such a process would lead to deuterium in only allylic or in both allylic and olefinic positions similar to the results in Figure 1. Dissociatively adsorbed olefin, XI,[11,12]

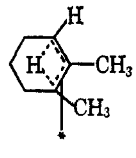


XI

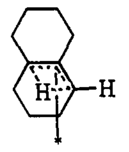
could produce cyclohexene with one deuterium on the double bond, and if the rate of dissociative exchange were the same as the rate of associative exchange (I–V in Figure 1) the results could be explained.

We would like to suggest that no existing mechanism satisfactorily explains these results and that they signal the presence of a previously unrecognized species on metal surfaces, a species capable of explaining many phenomena which occur during hydrogenation and exchange. The peculiar requirement of this species is its production of V and cyclohexene-1-*d* in approximately equal amounts. Such a species is XII, which could be either a separate intermediate or the transition state[13] for an intramolecular hydrogen shift as shown in Figure 3; it should rearrange to either XIII or XIV with equal ease.

Not only does XII satisfy the XIII = XIV requirement but it also offers help out of the top-addition difficulty;[2,10] *i.e.*, it can be produced from X by simple bottom side attack. Exchange of 1,1,3,3-tetramethylcyclohexane[10] could occur as shown for XV. *trans*-1,2-Dimethylcyclohexane from 1,2-dimethylcyclohexene[5] (XVI) and *trans*-decalin from 9,10-octalin (XVII) are readily explained as is the exchange of four positions in 9,10-octalin.[8]



XVI



XVII

Acknowledgments.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. One of us, J. R. S., is grateful for summer support from the National Science Foundation High School Teachers Research Participation Program.

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