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Mode of Hydrogen Attack during the Hydrogenation of Olefins

Hydrogenation and Isomerization of *cis*- and *trans*-Cyclodecene

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Hydrogenation and isomerization of *cis*- and *trans*-cyclodecene were studied at 3 atm and room temperature. *Trans* isomerizes to *cis* during hydrogenation and both compete for the same surface sites. After *trans* is consumed, hydrogenation of remaining *cis* is poisoned and proceeds at a rate only 60% that of *cis* which is originally devoid of *trans*. *Trans* hydrogenates almost as fast as this latter *cis*. Lower hydrogen pressures slow both hydrogenation and isomerization of *trans* but affect hydrogenation most. Results are explained in terms of the classical mechanism with hydrogen attacking from the surface to the "bottom side" of the chemisorbed molecules.

In the hydrogenation of certain sterically complicated olefins it is clear that predominant attack of hydrogen is at the side of chemisorbed carbon which faces metal catalysts (*1–4*). There exists evidence, however, that in simpler cases the attack may occur in some other manner (*5*) and the situation is not so clearly resolved. Of important bearing on the question is the suggestion (*5*) that the ready hydrogenation of *cis*- and *trans*-cyclononene (*6*) indicates that hydrogen attacks the side of the double bond facing the metal. Because of the geometry of *trans*-cycloolefins, chemisorbed *trans* would be sterically hindered for attack from above. The adsorbed *trans* form, however, could isomerize to *cis* by a step not involving hydrogen and the *cis* could be the only isomer to which hydrogen adds. This last possibility appeared reasonable from the report that *trans*-cyclononene and *trans*-cyclodecene, when formed during the hydrogenation of their respective 1,2-dienes, isomerize to their more thermodynamically stable *cis* isomers as the reaction proceeds (*7*). In view of these findings and because of the importance of these notions to our understanding of the nature of surface species, we have investigated the hydrogenation and *cis–trans* isomerization of *cis*- and *trans*-cyclodecene.

Experimental

The hydrogenations and isolations of the reaction mixtures were conducted as previously described for the Parr low-pressure hydrogenation apparatus (Parr Instrument Co.) (*8*). Matheson electrolytic hydrogen was used without further purification and a Neoprene stopper was used to connect the reaction flask to the apparatus. During the reaction the drop in pressure was never more than 0.2 psig. The olefins were kindly furnished by Dr. P. E. Fanta of these laboratories and were prepared by the procedure of Prelog (*9*). They consisted of four mixtures, as shown in Table 1. Analyses were performed on a 1 ft × ¼-inch

TABLE 1
COMPOSITIONS OF THE STARTING MIXTURES

Olefin	Mixture			
	A	B	C	D
trans-Cyclodecene	70.5 ± 0.8	90.3	96.9	0.0
cis-Cyclodecene	26.9 ± 0.7	9.7	3.1	89.2
Saturates[a]	2.6 ± 0.2	0.0	0.0	10.8

[a] Decalins and cyclodecane.

$AgNO_3$-triethylene glycol (60–80 mesh firebrick) gas chromatography column at 116°C (*10*). Errors in analyses were larger than usual (*8*), as shown by the average deviations in Table 1 of Mixture A. In every experiment, 0.20 cc of olefin was dissolved in 5.00 cc of glacial acetic acid (Allied Chemical, ACS, 99.7%). The platinum oxide catalyst was taken from a 5-g lot purchased from Goldsmith Brothers and coded No. 13410. It was dark brown in color and turned intense black within 15 sec after the start of each reaction. On no occasion did the catalyst clump during the reaction (*11*); however, in several experiments the filtrate of the reaction mixture was darkly colored. We do not know whether this was due entirely to colloidal Pt or to platinum complexes or a combination of both, but it was found that the addition of a couple of drops of saturated NaCl solution to the mixtures after reaction caused the catalyst to clump sufficiently so as not to pass through filter paper.

RESULTS

Two series of hydrogenations were conducted with two different starting mixtures to determine the extent of isomerization. The data in Table 2 were obtained with Mixture A; the numbers in parentheses were calculated after correcting for the 2.6% saturate in the starting mixture, i.e., 2.6% was subtracted from the % saturate and the percentages were normalized to total 100%. Table 3 shows the results of reducing Mixture B.

Two special experiments were conducted to determine if hydrogen was required for the isomerization. Catalyst was prereduced in glacial acetic acid under the usual conditions and then the reaction flask was evacuated (house vacuum, approx. 20 cm Hg) and Mixture C introduced through the Neoprene stopper by means of a syringe. In Experiment 14, under the same conditions as 13 but with longer time, considerably more isomerization occurred while almost the same amount of hydrogenation took place. Those results are shown in Table 4.

Two other experiments were performed, one with Mixture D to compare the relative rates of reduction of *cis* alone to the *cis–trans* mixtures, and one with Mixture C for comparison with the data in Tables 2 and 3. These data are in Table 5. Numbers in

TABLE 2
RESULTS OF PARTIAL HYDROGENATIONS OF MIXTURE A

Expt. No.	Catalyst (g)	Pressure (psig)	Time (min)	Saturate (%)	*cis*-Cyclodecene (%)	*trans*-Cyclodecene (%)
—	—	—	0	2.6 (0.0)	26.9 (27.6)	70.5 (72.4)
3	0.0209	32.0	1	29.7 (27.8)	39.6 (40.7)	30.7 (31.5)
2	0.0222	32.2	2	59.2 (58.1)	39.7 (40.8)	1.1 (1.1)
4	0.0214	32.1	3	80.9 (80.4)	19.1 (19.6)	0.0 (0.0)
1	0.0211	32.2	5	99.3 (99.3)	0.7 (0.7)	0.0 (0.0)

TABLE 3
RESULTS OF PARTIAL HYDROGENATIONS OF MIXTURE B

Expt. No.	Catalyst (g)	Pressure (psig)	Time (min)	Saturate (%)	*cis*-Cyclodecene (%)	*trans*-Cyclodecene (%)
—	—	—	0	0.0	9.7	90.3
10	0.0216	32.4	0.5	8.6[a]	16.5[a]	75.0[a]
7	0.0216	32.3	1.0	30.7	26.1	43.3
8	0.0216	32.2	1.5	42.3	29.4	28.3
9	0.0217	32.4	2.5	66.7	29.6	3.7
11	0.0217	32.4	2.75	72.9	26.2	0.9
12	0.0217	32.3	4.0	92.1	7.9	0.0

[a] Poor analysis.

parentheses are corrected for the existence of 10.8% saturate in D.

DISCUSSION

Rates

The best rate data we could obtain with this apparatus are shown in Table 3, for Mixture B. Plotting the per cent cyclodecane from these data in the manner shown in Fig. 1 indicates that approximately 8% reduction occurred before shaking was started, i.e., cyclodecane extrapolates to negative time at 0% reduction. Since visual observation suggested that the catalyst was not fully reduced until a few seconds after shaking was started, it seems reasonable to expect a small initiation period. Apparently the pre-reaction procedure of evacuating and filling with hydrogen resulted in some catalyst reduction followed by olefin reduction.

TABLE 4
RESULTS OF PARTIAL HYDROGENATIONS OF MIXTURE C *in vacuo*

Expt. No.	Catalyst (g)	Time (min)	Saturate (%)	*cis*-Cyclodecene (%)	*trans*-Cyclodecene (%)
—	—	0	0.0	3.1	96.9
13	0.0204	5	25.0	30.0	45.0
14	0.0202	15	27.8	44.8	27.4

Assuming that the data from the other experiments would extrapolate to the same

TABLE 5
REDUCTION OF MIXTURES C AND D

Expt. No.	Mix	Catalyst (g)	Pressure (psig)	Time (min)	Saturate (%)	*cis*-Cyclodecene (%)	*trans*-Cyclodecene (%)
5	C	0.0213	32.4	2	61.9	31.3	6.8
6	D	0.0214	32.4	2	75.5 (72.5)	24.5 (27.5)	0.0

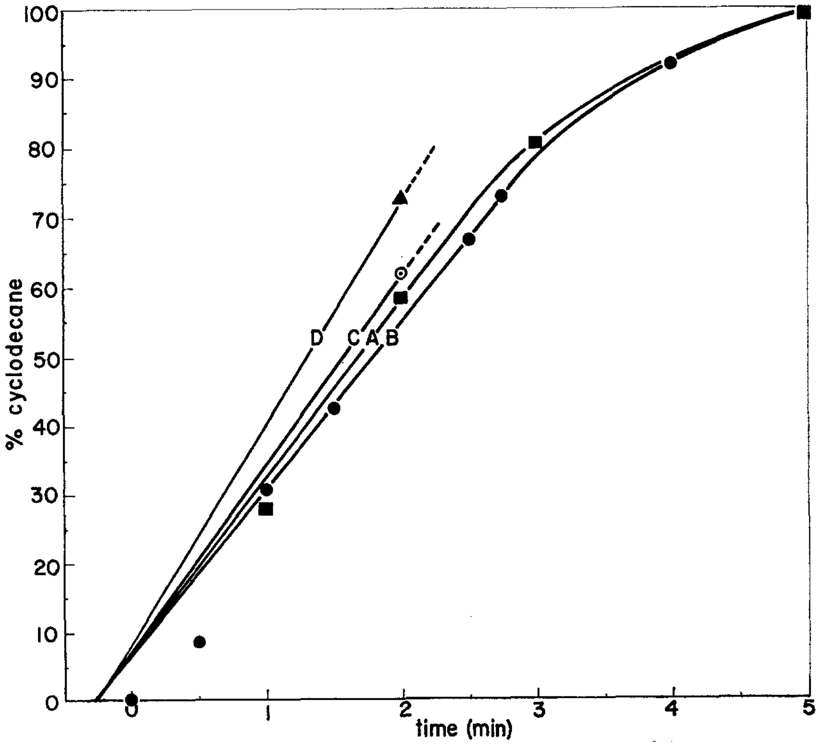

FIG. 1. Hydrogenations of the cyclodecenes: ■, A; ●, B; ⊙, C; and ▲, D.

TABLE 6
RATES OF HYDROGENATION OF *cis*- AND *trans*-CYCLODECENE[a]

Mixture[b]	Rates[c]
A	1162
B	1134
C	1291
Average of A, B, and C	1196 ± 64
D	1505

[a] Slopes of cyclodecane lines in Fig. 1 normalized to 1 g of catalyst.

[b] See Table 1.

[c] Expressed as per cent increase of cyclodecane in the hydrocarbon fraction per gram of catalyst per minute (i.e., % sat/g cat min).

time as the data from Mixture B, similar lines were constructed for reductions with Mixtures A, C, and D (Fig. 1). The slopes of these lines, corrected for differences in catalyst weight give an estimate of the relative rates of reduction of *cis*- and *trans*-cyclodecene and are shown in Table 6. The *cis* rate is 1.26 times the average rate for the three *trans* hydrogenations and 1.32 times the rate for B. The average deviation of A, B, and C indicates a 5.4% error but the total deviation from the average suggests a 13% error in the rates. The *cis* rate is outside of this larger error, and it seems safe to consider the *cis* to hydrogenate at least as fast and probably faster than *trans*. More precise techniques will be required to establish this with certainty (*12*).

That complicating factors may obscure the data is evidenced by the low rate of hydrogenation of the *cis* produced during the reduction of A and B (Fig. 2). The rate of decrease of the *cis* in A and B is only 60% of the rate of *cis* in D. It could be argued that this is due to diffusional control of the reaction. Such limiting by diffusion would have to be due to reduction in concentration of olefin since the hydrogen concentration is essentially constant throughout the reaction. There is a significant lowering of rate after about 3 min; however, before that time the rate of reduction of *cis* in A and B appears to be constant. It seems reasonable then to attribute the lower rate before 3 min to another factor.

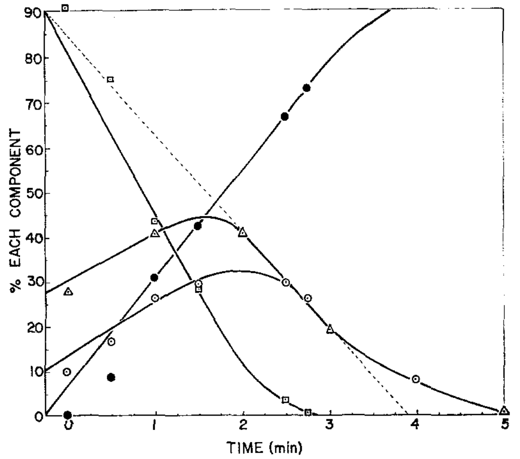

FIG. 2. Hydrogenations of Mixture B showing correlation with *cis* made in A: ●, cyclodecane; ⊡ is *trans;* and *cis* is represented by ⊙ for B and ⚠ for A.

Reductions of *cis* produced in A and B are comparable to performing consecutive experiments on the same catalyst. In such experiments platinum catalysts may become partially poisoned during hydrogenation so that a series of hydrogenations of the same compound on the same catalyst will yield a series of decreasing rates (*12*). It is not entirely clear, however, why the rate of hydrogenation of *trans* should not gradually decrease if the surface is becoming poisoned. It may be that the *trans* excludes both the poison and *cis* from the surface so that after the *trans* is consumed the poison affects the rate of *cis* reduction. This poison could be the peroxide of one of the isomers (*12, 13*), a possibility which was not investigated.

Another possible explanation of the slower reduction of *cis* in A and B could be related to the relative stabilities of metal-olefin complexes (*14*). For these olefins the *trans* isomer forms the more stable silver complex and presumably would also form the more stable platinum complex. If unhydrogenated *trans* residues covered approximately half of the active surface then the observed rate for the *cis* might be expected. Some of the requirements that such a *trans* residue would have to meet are (1) it must not be readily hydrogenated in the presence of *cis*, (2) it must not be displaced by *cis*, and (3) it must be displaced by *trans*. Further speculation about this species does not seem appropriate on the basis of this evidence.

Examination of the data plotted in Fig. 2 sheds light on the competition between *cis* and *trans* for surface sites. That production of saturate is zero order when both *cis* and *trans* are being hydrogenated suggests that a common step is rate-limiting. The fact that *cis* begins to take up hydrogen before all *trans* is consumed indicates that there is mutual competition for the same surface sites. The situation seems to be, then, one in which *cis* and *trans* compete for the same surface sites but go through some common rate-determining step along the path to saturate.

Reduced Pressure

Isomerization might occur through steps not involving hydrogen. To investigate this possibility experiments were performed under reduced pressure, as shown in Table 4. In Experiment 13 the reaction was allowed to proceed for 5 min before analysis, but in Experiment 14 the reaction time was 15 min. Virtually all available hydrogen was consumed in the first 5 min, as shown by the very small additional production of saturate in Experiment 14. A third experiment demonstrated that the acetic acid solvent does not isomerize the olefins under the reaction conditions. These data, when compared to B, are particularly revealing. With B the initial ratio of isomerization to hydrogenation is 0.47 and, within the large experimental error, A is the same. The ratio under reduced pressure, however, is 5.3 and shows its high dependence on the surface hydrogen concentration. However, even though the ratio of isomerization to hydrogenation increased approximately 10-fold, both reactions are slower. The rate of isomerization is only 14% of that with B. Since both paths are slowed, both must depend on hydrogen in some step.

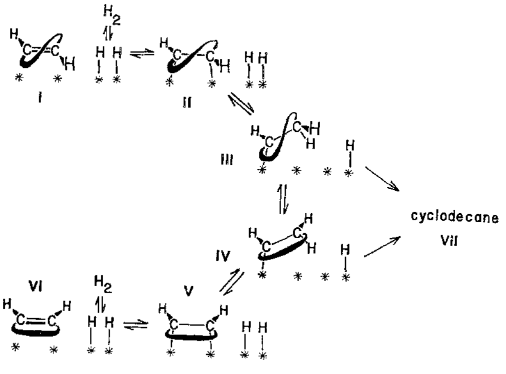

FIG. 3. Classical mechanism for isomerization and hydrogenation of *cis*- and *trans*-cyclodecene. Curved lines represent $(\text{–CH}_2\text{–})_8$. Asterisks represent surface sites.

Mechanism

All of these observations appear to be readily accommodated in the classical Horiuti-Polanyi half-hydrogenated-state mechanism as detailed in Fig. 3. Path I–VI and back accounts for isomerization, paths I–II–III–VII and VI–V–IV–VII lead to hydrogenation. Step II–III consumes hydrogen but step IV–V gives it back and *vice versa*. Steps III–VII and IV–VII consume hydrogen irreversibly (*5*).

The constant rate of production of cyclodecane when both *cis* and *trans* are being consumed is explained if III–IV is rapid compared to III–VII and/or IV–VII. VI is much more thermodynamically stable than I (*10*); the equilibrium ratio at 25°C is about 30. IV must also be considerably lower in energy content than III, so IV should predominate and equilibration should be rapid since only internal rotation is required.

Greater dependence of hydrogenation than of isomerization on hydrogen pressure is explained because hydrogenation requires the addition of two surface hydrogens and isomerization requires only the presence of some hydrogen on the surface (*8*). If steps III–VII and IV–VII were blocked, isomerization should continue to equilibrium even in the presence of traces of hydrogen. In fact we find in studies with *cis*- and *trans*-cyclododecene that CCl_4 greatly inhibits these last steps on palladium and that surface hydrogen is used over and over again in the isomerization (*15*). These data, then, disclose little reason to postulate anything more than in Fig. 3 to account for isomerization. This, it has been pointed out, indicates that at least addition of the first hydrogen (Step II–III) must be from the surface to the side of the double bond facing the surface (*16*). The only evidence we can offer in support of hydrogen addition to the "top side" is the apparently greater rate in D than in A, B, and C.

In view of these data, the finding of *trans* during hydrogenations of 1,2- and 1,3-cyclodecadienes is an important mechanistic clue (*7*). If III were formed it would most probably form IV before II; therefore, desorption of *trans* signals the absence of III and rejects addition of molecular hydrogen or simultaneous addition of two hydrogens (*17*). If hydrogen adds to the left end of species VIII in Fig. 4, something equivalent to IX or II must be formed. Both could desorb to give *trans* and the data do not distinguish between them.

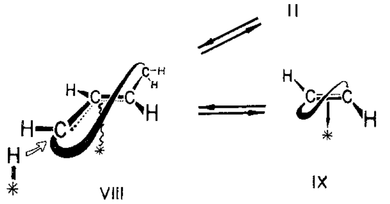

FIG. 4. Hydrogenation of Moore's intermediate.

Currently, species like IX are being emphasized as possible intermediates in the hydrogenation mechanism (*14*), and the analogy to known metal-olefin complexes is enticing. It is possible that they may offer some advantages over the classical mechanism. They make sense as alternatives to species like II and V, especially if only one metal atom can be considered to be involved (*18*). They may represent a separate pathway, e.g., I–IX–III, which is more likely to occur on one metal than another.

CONCLUSIONS

The classical mechanism seems to account for all of the results except two: they are the slightly faster hydrogenation of *cis* than *trans* and the slow hydrogenation of *cis* produced from *trans*. The first suggests that a small amount of "top-side" addition may be occurring; however, the datum is not conclusive. The second may be due to an unknown poison, possibly *trans* residues. Under these conditions hydrogen adds almost exclusively from the surface to the surface side of chemisorbed molecules.

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REFERENCES

1. BLADON, P., HENBEST, H. B., JONES, E. R. H., LOVELL, B. J., WOOD, G. W., ELKS, J., EVANS, R. M., HATHWAY, D. E., OUGHTON, J. F., AND THOMAS, G. H., *J. Chem. Soc.*, p. 2921 (1953).
2. BREAM, J. B., EATON, D. C., AND HENBEST, H. B., *J. Chem. Soc.*, p. 1974 (1957).
3. BRODIE, H. J., HAYANO, M., AND GUT, M., *J. Am. Chem. Soc.* **84,** 3766 (1962).
4. RINGOLD, H. J., GUT, M., HAYANO, M., AND TURNER, A., *Tetrahedron Letters* (No. 18), 835 (1962).
5. BURWELL, R. L., JR., *Chem. Revs.* **57,** 895 (1957).
6. BLOMQUIST, A. T., LIU, L. H., AND GOHRER, J. C., *J. Am. Chem. Soc.* **74,** 3643 (1952).
7. MOORE, W. R., *J. Am. Chem. Soc.* **84,** 3788 (1962).
8. SIEGEL, S., AND SMITH, G. V., *J. Am. Chem. Soc.* **82,** 6082 (1960).
9. PRELOG, V., SCHENKER, K., AND GUNTHARD, H. H., *Helv. Chim. Acta* **35,** 1598 (1952).
10. COPE, A. C., MOORE, P. T., AND MOORE, W. R., *J. Am. Chem. Soc.* **82,** 1744 (1960).
11. SMITH, G. V., AND BURWELL, R. L., JR., *J. Am. Chem. Soc.* **84,** 925 (1962).
12. HUSSEY, A. S., BAKER, R. H., AND KEULKS, G. W., *Abstracts of Papers presented at the 148th Meeting, American Chemical Society,* p. 60s (September, 1964).
13. BURWELL, R. L., JR., AND LONER, C. J., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* p. 808 (North-Holland Publ. Co., 1965.
14. ROONEY, J. J., AND WEBB, G., *J. Catalysis* **3,** 488 (1964).
15. SMITH, G. V., AND MENON, M. C., unpublished data.
16. BURWELL, R. L., JR., personal communication.
17. FARKAS, A., AND FARKAS, L., *Trans. Faraday Soc.* **33,** 837 (1937).
18. BOND, G. C., AND WELLS, P. B., *Advan. Catalysis* **15,** 91 (1965).