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Competitive Hydrogenations on Platinum

ALLEN S. HUSSEY, ROBERT H. BAKER, AND GEORGE W. KEULKS

From the Ipatieff Laboratory, Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

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The results of the competitive hydrogenation of 14 pair combinations of 10 cycloalkenes from solution in cycloalkane solvents on alumina-supported platinum catalysts at 25.0° and 1 atm are reported. The results are found to be in accord with both equilibrium and rate-controlled chemisorption models. The latter is preferred. The stereochemical problems represented by the formation of *trans*-dimethylcyclohexanes from the xylenes and the pressure-variable *cis/trans* product ratio from dialkylcycloalkenes are discussed in terms of these results.

Some of the factors which influence chemisorption of cycloalkenes on platinum surfaces are considered.

INTRODUCTION

We have recently reported results of a study of the kinetics of the hydrogenation of cycloalkenes from solution in cyclohexane on alumina-supported platinum catalysts (*1*). We report here the results of experiments in which pair combinations of many of the same cycloalkenes have been hydrogenated under the same conditions. These competitive hydrogenations were carried out in the hope that the results might shed some light on the factors which control the chemisorption of alkenes on platinum surfaces. It was also hoped that such information might lead in turn to a better understanding of the stereochemical results observed in the special competitive situation where geometric isomers are formed (e.g., 1,4-dimethylcyclohexene → *cis*- and *trans*-1,4-dimethylcyclohexane) (*2*).

EXPERIMENTAL

Apparatus, reactants, solvents, and catalysts. The apparatus used was that described previously (*1*). The alkenes and solvents were rigorously purified and percolated through alumina under nitrogen immediately before use as before to ensure the absence of rate-influencing impurities. The catalyst for a particular experiment was chosen from the several at hand of varying specific activity (*1*) so that 20–40 mg gave convenient hydrogen uptake rates of 1–3 ml min^{-1}.

Procedure. In a typical experiment, 0.200 ml of an approximately equimolar mixture of rigorously purified cyclohexene and cycloheptene was injected into the hydrogenation flask containing 37.88 mg of a 0.52% platinum-alumina catalyst and 0.40 ml of cyclopentane. Agitation at 25.0° ± 0.1°C under a constant (± 1 mm) hydrogen pressure of 757 mm was interrupted periodically to permit removal of a sample for analysis by gas chromatography. Several experiments with overlapping points furnished composition vs. percent hydrogenation data as shown in Table 1.

Data for the competitive hydrogenation of 13 other pairs of cycloalkenes were obtained from similar replicate hydrogenation experiments. A doubling of the amount of catalyst had a proportionate effect on the rates of hydrogen absorption but did not change the relative rate at which each of a pair of cycloalkenes was hydrogenated, nor did the use of catalysts differing in platinum content.

Analytical procedure. The samples removed for analysis were completely separated into solvent, cycloalkene, and cycloalkane

TABLE 1

COMPETITIVE HYDROGENATION OF CYCLOHEXENE AND CYCLOHEPTENE[a]

Mole % Composition			
C_6-ene	C_6-ane	C_7-ene	C_7-ane
45.2	0.0	54.8	0.0
42.6	2.6	44.5	10.3
40.6	4.6	38.2	16.6
38.0	7.3	26.2	28.5
34.6	10.6	17.4	37.4
30.1	15.2	9.0	45.7
20.1	25.2	1.6	53.2
15.7	29.7	0.0	54.6
3.2	42.0	0.0	54.8

[a] In cyclopentane at 757 mm, 25.0°, 0.52% platinum catalyst.

components by gas chromatography. The compositions were estimated from peak areas calculated from peak heights and half-peak widths as measured on the strip-chart recording using vernier calipers. The gas-liquid phase chromatography columns and conditions used to separate the several mixtures into the five components to give symmetrical peaks are summarized in Table 2.

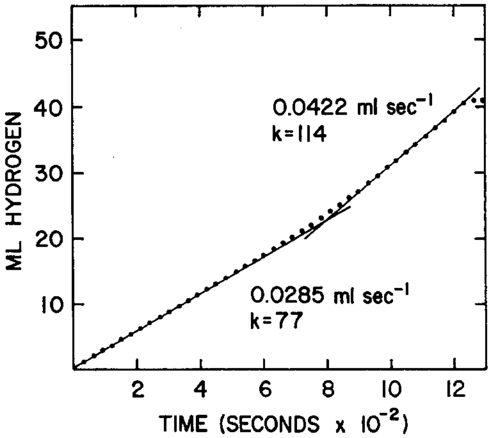


FIG. 1. Rate of hydrogen absorption: 0.84 mmoles of cyclohexene and 0.85 mmoles cycloheptene in cyclohexane, 33.93 mg of 0.52% Pt catalyst, 761 mm, 25.0°; k in moles min^{-1} g $atom^{-1}$ atm^{-1}.

Hydrogen absorption rates. In several rate experiments of the type described earlier (*1*), a mixture of two cycloalkenes was hydrogenated as the intermediate sample between two samples of cyclohexene without interrupting the hydrogenation to remove samples for analysis.

TABLE 2

ANALYSIS OF HYDROGENATION MIXTURES BY GAS CHROMATOGRAPHY

A vs. B[a]		Solvent[b]	Column[c]	Temp.[d]	Flow rate[e]
C_5	1-MeC_5	CH	1	65°	75
C_5	C_6	MCH	2	80°	85
C_5	C_7	CH	3	60–175°	120
C_5	C_8	CH	3	60–200°	120
C_6	1-MeC_5	CP	1	65°	75
C_6	1-MeC_6	CP	4	70–125°	100
C_6	3-MeC_6	CP	3	110°	85
C_6	4-MeC_6	CP	3	110°	85
C_6	4,4-DiMeC_6	CP	2	70°	45
C_6	C_7	CP	3	75–175°	120
C_6	C_8	CP	3	75–200°	120
4-MeC_6	4,4-DiMeC_6	CH	2	80°	45
C_7	1-MeC_7	CH	2	90°	45
C_7	C_8	CH	3	75–200°	120

[a] C_5 is cyclopentene; 1-MeC_5 is 1-methylcyclopentene, etc.

[b] CH is cyclohexane, CP is cyclopentane; MCH is methylcyclohexane.

[c] Columns are as follows: 1, 33% tetramethylene sulfone on 100/120 mesh C-22 firebrick, 12 ft; 2, 15% diethylene glycol succinate polyester on 100/120 mesh C-22 firebrick, 25 ft; 3, 20% Dow-Corning #200 silicone oil on 60/80 mesh Chromosorb P, 22 ft; 4, 10% Dow-Corning #550 silicone oil on 110/120 mesh C-22 firebrick, 10 ft.

[d] Constant temperature or programmed at 4° per min through range indicated.

[e] Helium, ml per min.

The data from such an experiment (33.93 mg of 0.52% Pt catalyst) using a mixture of cyclohexene (0.84 mmoles) and cycloheptene (0.85 mmoles) are plotted in Fig. 1.

RESULTS

The composition vs. percent hydrogenation data for the several pairs of cycloalkenes were obtained by gas-liquid chromatographic analysis of samples removed at several stages in the hydrogenations. We programmed the removal of samples for analysis from replicate experiments to give overlapping data points to improve reliability. The data for a cyclohexene-cycloheptene mixture given in Table 1 are an example. Conditions for the several analyses are summarized in Table 2.

The rates of hydrogen absorption for several pairs of these cycloalkenes were measured also. In these experiments, the mixtures were injected as intermediate samples between two samples of cyclohexene in cyclohexane, the identical rates of hydrogenation of the two bracketing samples of cyclohexene serving to guarantee the absence of rate-slowing impurities (*1*). The results observed for a mixture of cyclohexene and cycloheptene are presented in Fig. 1. The initial rate is that for cycloheptene separately; the final rate, that for cyclohexene (*1*). Rate plots for other mixtures exhibited a greater curvature upward (e.g., cyclohexene-cyclooctene) or downward (e.g., cyclopentene-cycloheptene), depending upon the degree of selectivity and the differences in the separate rates of hydrogenation of the two components. It therefore appears that the surface reactions of one component do not interfere with the surface reactions of the other; hence, the hydrogenation of mixed cycloalkenes can properly be treated as a competitive reaction.

In competitive reactions such as we are concerned with here, A and B compete for reaction with C in accord with their molar concentrations and the reaction constants which govern the separate reactions. An *equilibrium chemisorption* model has been developed by Wauquier and Jungers (*3*) for the special situation where A and B are aromatic hydrocarbons and C is a heterogeneous catalyst. This treatment has more recently been applied by Smith and coworkers (*4*) in studies of a large number of aromatic compounds. The chemisorption of aromatic hydrocarbons A and B are assumed to follow the Langmuir isotherm. When conditions are such that the overall reactions are first order in the amount of catalyst, then

$$d[\mathrm{A}]/d[\mathrm{B}] = k_\mathrm{A}b_\mathrm{A}[\mathrm{A}]/k_\mathrm{B}b_\mathrm{B}[\mathrm{B}] \quad (1)$$

where k_A and k_B are the overall rate constants for the two hydrogenation reactions, b_A and b_B are the equilibrium constants for the chemisorptions, and [A] and [B] are the respective molar concentrations. Integration of Eq. (1) leads to

$$\frac{\log [\mathrm{A}_0]/[\mathrm{A}]}{\log [\mathrm{B}_0]/[\mathrm{B}]} = k_\mathrm{A}b_\mathrm{A}/k_\mathrm{B}b_\mathrm{B} = k_\mathrm{A}K_\mathrm{AB}/k_\mathrm{B} \quad (2)$$

where K_AB is the equilibrium constant for the process

$$\mathrm{A(in\ solution)} + \mathrm{B(adsorbed)} \rightleftarrows \mathrm{A(adsorbed)} + \mathrm{B(in\ solution)}$$

A linear log [A] vs. log [B] plot implies agreement with this model. Multiplication of the slopes of such plots by $k_\mathrm{B}/k_\mathrm{A}$ furnishes values for K_AB and thence relative values for the chemisorption constants for the several hydrocarbons if an arbitrary value is chosen for one of them (*4*).

However, if the fractions of the surface occupied by A and B are controlled by the *rate of chemisorption* of A vs. B, then

$$d[\mathrm{A}]/d[\mathrm{B}] = k_{2\mathrm{A}}[\mathrm{A}]/k_{2\mathrm{B}}[\mathrm{B}] \quad (3)$$

where $k_{2\mathrm{A}}$ and $k_{2\mathrm{B}}$ are the rate constants for the chemisorption of A and B, respectively. Since Eq. (3) and its integral

$$\frac{\log [\mathrm{A}_0]/[\mathrm{A}]}{\log [\mathrm{B}_0]/[\mathrm{B}]} = k_{2\mathrm{A}}/k_{2\mathrm{B}} \quad (4)$$

are of the same form as Eq. (1) and Eq. (2), it is obviously not possible to choose between the *equilibrium chemisorption* model (*3*, *4*) and its *rate of chemisorption* counterpart on the basis of the results of the competitive reactions alone.

The data of Table 1 are plotted in Fig. 2. Similar plots of the data obtained from

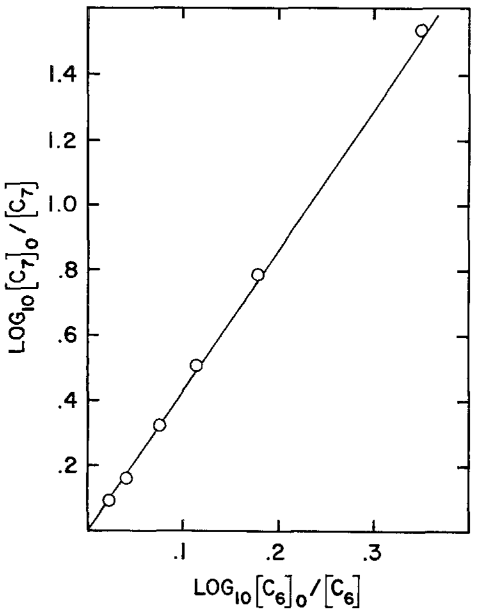


FIG. 2. Logarithmic plot of disappearance of cycloheptene vs. cyclohexene, data of Table 1.

other pairs of cycloalkenes were also linear and furnished values for the slopes which are summarized in Table 3. The last three columns of Table 3 list the specific reaction rates for the cycloalkenes (*1*) and values for K_{AB} for the several pairs as calculated from Eq. (2).

According to the rate of chemisorption model, the slopes listed in Table 3 correspond to k_{2A}/k_{2B}, the ratio of the rate constants for chemisorption. These are better compared, as are also the equilibrium K_{AB} values, if they are converted to relative values. These are summarized in Table 4 based on cyclohexene equal to 10.0 for both sets. The values in parentheses for the first three cycloalkenes involve data from the cyclooctene-cyclohexene system where the very surprising preferential hydrogenation of cyclooctene over cyclohexene was observed repeatedly. We conclude that cyclooctene exhibits a unique interference with the chemisorption of cyclohexene but we cannot offer any reason why this occurs.

DISCUSSION

We have recently proposed that the chemisorption of most cycloalkenes on hydrogenation sites (as distinguished from olefin exchange sites) of platinum surfaces near room temperature and 1 atm of hydrogen is effectively irreversible (*1*). [Tetrasubstituted cycloalkenes (e.g., 1,

TABLE 3

SELECTIVITY IN THE COMPETITIVE HYDROGENATIONS OF CYCLOALKENES[a]

A[b]	B[b]	Slope log[A]/log[B]	k_A[c]	k_B[c]	K_{AB}[d]
C_5	1-MeC_5	20.0	121	85	14.0
C_5	C_6	8.0	121	113	7.5
C_5	C_7	2.2	121	78	1.4
C_5	C_8	8.2	121	10	0.68
C_6	1-MeC_5	1.8	113	85	1.4
C_6	1-MeC_6	20.0	113	57	10.0
C_6	3-MeC_6	1.6	113	103	1.5
C_6	4-MeC_6	1.4	113	94	1.2
C_6	4,4-DiMeC_6	2.3	113	100	2.0
C_7	C_6	4.3	78	113	6.3
C_7	1-MeC_7	20.0	78	34	8.7
C_7	C_8	4.9	78	10	0.63
C_8	C_6	2.2	10	113	25
4-MeC_6	4,4-DiMeC_6	2.0	94	100	2.1

[a] In cyclopentane, cyclohexane, or methylcyclohexane; between 755 and 765 ± 1 mm; 25.0° ± 0.1°; 0.52% Pt on alumina.

[b] C_5 is cyclopentene, 1-MeC_5 is 1-methylcyclopentene, etc.

[c] Specific reaction rate for A and B; see ref. (*1*).

[d] Equilibrium constants for the competitive chemisorption of A and B calculated from Eq. (2); see refs. (*3*) and (*4*).

TABLE 4

COMPARISON OF RELATIVE RATES OF CHEMISORPTION AND RELATIVE EQUILIBRIUM CHEMISORPTION CONSTANTS FOR CYCLOALKENES ON PLATINUM

Cycloalkene[a]	Relative rate[b]	Relative equilibrium[b]	k^c
C_5	80, 95, 112, (180)	75, 83, 99, (170)	121
C_7	43, 36, (108)	60, 54, (160)	78
C_8	(22), 8.9, 9.8	(250), 110, 94	10
C_6	10.0	10.0	113
4-MeC_6	7.1, 8.7	8.3, 10.0	94
3-MeC_6	6.3	6.7	103
1-MeC_5	5.6, 4.0	7.1, 5.4	85
4,4-DiMeC_6	4.3, 3.6	6.8	100
1-MeC_7	2.1	5.0, 4.0	34
1-MeC_6	0.50	1.0	57

[a] See legend for Table 2.

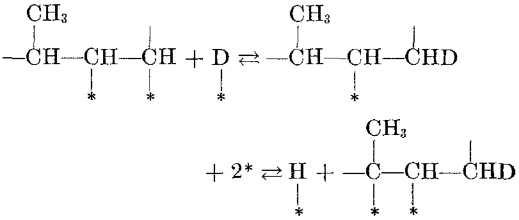
[b] Based on cyclohexene = 10.0.

[c] Specific reaction rate; see ref. (*1*).

2-dimethylcyclohexene and $\Delta^{9,10}$-octahydronaphthalene) and certain others for which facile pathways for isomerization exist (e.g., ethylidenecyclopentane and *trans*-cyclodecene) are probably exceptions.] In the first place, the rates of hydrogenation of some 18 cycloalkenes all exhibit a zero order dependency on the concentration of the cycloalkene (*1*) under conditions in which a first order dependency on the amount of catalyst is observed (i.e., where transport of hydrogen into the liquid phase cannot be rate-limiting). In terms of the Langmuir isotherm, these kinetics require very strong chemisorption of the alkene such that the catalyst is saturated with respect to the substrate throughout the hydrogenation; hence if desorption does occur, the rate must be very small relative to the rate of adsorption.

More to the point, we were unable to observe any isomerization of thermodynamically unstable cycloalkenes to their more stable (*5*) and more slowly hydrogenated counterparts (e.g., 3-methylcyclopentene and 3-methylcyclohexene to their 1-methyl isomers) even though our gas-liquid chromatography analytical procedure would easily have revealed the presence of as little as 0.1% of such isomers.

Extensive exchange of protium by deuterium is observed under these conditions (*6*). This requires step (3) of the Horiuti-Polanyi mechanism for hydrogenation (*7*) not only to be reversible but to lead to a succession of monoadsorbed and diadsorbed surface species, as follows:



$$-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\underset{*}{\underset{|}{\mathrm{C}}}\mathrm{H}-\underset{*}{\underset{|}{\overset{|}{\mathrm{C}}}}\mathrm{H}+\underset{*}{\underset{|}{\mathrm{D}}}\rightleftarrows-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\underset{*}{\underset{|}{\mathrm{C}}}\mathrm{H}-\overset{|}{\mathrm{C}}\mathrm{HD}$$

$$+2^{*}\rightleftarrows\underset{*}{\underset{|}{\mathrm{H}}}+-\underset{*}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\underset{*}{\underset{|}{\mathrm{C}}}\mathrm{H}-\overset{|}{\mathrm{C}}\mathrm{HD}$$

If any significant amount of 1,2-diadsorbed alkane were to desorb from platinum surfaces, one would expect considerable 3-methylcyclohexene, for example, to be returned to the solution as its 1-methyl isomer. The latter would rapidly accumulate because it is not only more slowly hydrogenated but also is very effectively excluded from readsorption by its precursor (Table 3). Hence we conclude that chemisorption of cycloalkenes on the hydrogen addition sites of platinum surfaces is an irreversible process and we prefer the rate of chemisorption model [Eq. (3) and Eq. (4)] for the competitive hydrogenations reported here.

It has been proposed that desorbed cyclohexenes are key intermediates in the hydrogenation of aromatic hydrocarbons (*8*) and very small amounts of these (0.002 mole % with platinum) have since been detected (*9*). Somewhat larger but still small amounts have been detected when rhodium and, particularly, ruthenium catalysts have been used (*10*, *11*). The question is whether these are key intermediates or the result of incidental pathways of minor importance (*9–11*). A kinetic argument has been used to support the latter view (*10*, *11*b). An opposite argument (*9*, *11*a) is that intraparticle diffusion limitations prevent the return of more than traces of the intermediate cyclohexenes to the bulk solution, but that these are nevertheless key intermediates in the hydrogenation of arenes. Our interpretation of the competitive hydrogenation of cycloalkenes reported here supports the contention that desorbed cycloalkenes are incidental in the hydrogenation of arenes on platinum (*10*, *11*b), and that some alternative pathway leads directly from chemisorbed xylenes to almost all of the *trans*-dimethylcyclohexanes observed *without the intervention of desorption of tetrahydroarene intermediates.*

It also follows from our choice of a rate of chemisorption selectivity on platinum that we do not view the pressure-variable *cis/trans* product ratio from dialkylcyclohexenes to be the result of *equilibrium* chemisorption at low hydrogen pressures and of *irreversible* chemisorption at high (*12*). However, we do agree that the *cis/trans* ratio observed at high pressures generally reflects k_{2c}/k_{2t}, the ratio of the rate constants for the two modes of chemisorption, while the low pressure ratio does not (*12*). We simply propose that a surface reaction

$$\textit{cis}\text{-A} \rightleftarrows \text{symmetrical-A} \rightleftarrows \textit{trans}\text{-A}$$

approaches equilibrium at low hydrogen pressures but becomes decreasingly important as the pressure increases.

According to this proposal a cycloalkene A which forms *cis* and *trans* products, H_2A, chemisorbs irreversibly to give *cis*-A(ads) and *trans*-A(ads), but these are interconvertible by way of a symmetrical intermediate *on the surface.* At low pressure the relatively slow formation of product occurs when the reversible addition of the first hydrogen to give *cis*-HA(ads) or *trans*-HA(ads) is followed by associative desorption of the monoadsorbed alkane intermediate, as in the following sequence:

$$\text{A} + \text{catalyst} \xrightarrow{k_{2c}} \textit{cis}\text{-A(ads)}$$

$$\text{A} + \text{catalyst} \xrightarrow{k_{2t}} \textit{trans}\text{-A(ads)}$$

$$\textit{cis}\text{-A(ads)} \underset{k_{tc}}{\overset{k_{ct}}{\rightleftarrows}} \textit{trans}\text{-A(ads)}$$

$$\textit{cis}\text{-A(ads)} \underset{k_{-3c}}{\overset{k_{3c}}{\rightleftarrows}} \textit{cis}\text{-HA(ads)}$$

$$\textit{cis}\text{-HA(ads)} + \text{H(ads)} \xrightarrow{k_{4c}} \textit{cis}\text{-H}_2\text{A}$$

$$\textit{trans}\text{-A(ads)} + \text{H(ads)} \underset{k_{-3t}}{\overset{k_{3t}}{\rightleftarrows}} \textit{trans}\text{-HA(ads)}$$

$$\textit{trans}\text{-HA(ads)} + \text{H(ads)} \xrightarrow{k_{4t}} \textit{trans}\text{-H}_2\text{A}$$

We define the several fractions (θ) of the surface with suitable subscripts (Ac for 1,2-diadsorbed *cis*-alkane: HAt for 1-monoadsorbed *trans*-alkane, etc.: H for hydrogen: and MT for vacant) such that

$$\theta_{\mathrm{H}} + \theta_{\mathrm{A}c} + \theta_{\mathrm{A}t} + \theta_{\mathrm{HA}c} + \theta_{\mathrm{HA}t} + \theta_{\mathrm{MT}} = 1 \qquad (5)$$

The steady state assumption leads to

$$d\theta_{\mathrm{A}c}/dt \cong 0 = k_{2c}[\mathrm{A}]\theta_{\mathrm{MT}} - k_{ct}\theta_{\mathrm{A}c} + k_{tc}\theta_{\mathrm{A}t} - k_{3c}\theta_{\mathrm{A}c}\theta_{\mathrm{H}} + k_{-3c}\theta_{\mathrm{HA}c} \qquad (6)$$

and

$$d\theta_{\mathrm{HA}c}/dt \cong 0 = k_{3c}\theta_{\mathrm{A}c}\theta_{\mathrm{H}} - k_{-3c}\theta_{\mathrm{HA}c} - k_{4c}\theta_{\mathrm{HA}c}\theta_{\mathrm{H}} \qquad (7)$$

with equivalent expressions for the *trans* counterparts. Equations (6) and (7) lead to

$$\theta_{\mathrm{HA}c} = \frac{k_{3c}\theta_{\mathrm{H}}[k_{tc}\theta_{\mathrm{A}t} + k_{2c}(\mathrm{A})\theta_{\mathrm{MT}}]}{k_{ct}k_{-3c} + k_{ct}k_{4c}\theta_{\mathrm{H}} + k_{3c}k_{4c}\theta_{\mathrm{H}}^2} \qquad (8)$$

and the expressions for the *trans* counterparts to

$$\theta_{\mathrm{HA}t} = \frac{k_{3t}\theta_{\mathrm{H}}[k_{ct}\theta_{\mathrm{A}c} + k_{2t}(A)\theta_{\mathrm{MT}}]}{k_{tc}k_{-3t} + k_{tc}k_{4t}\theta_{\mathrm{H}} + k_{3t}k_{4t}\theta_{\mathrm{H}}^2} \qquad (9)$$

From the rate expression

$$d[\mathrm{H_2A}]/dt = k_4\theta_{\mathrm{HA}}\theta_{\mathrm{H}} \qquad (10)$$

$$d[cis]/d[trans] = k_{4c}\theta_{\mathrm{HA}c}/k_{4t}\theta_{\mathrm{HA}t} \qquad (11)$$

whence [from Eqs. (8), (9), and (11)]

$$\frac{d[cis]}{d[trans]} = \frac{k_{3c}k_{4c}[k_{tc}\theta_{\mathrm{A}t} + k_{2c}(\mathrm{A})\theta_{\mathrm{MT}}][k_{tc}k_{-3t} + k_{tc}k_{4t}\theta_{\mathrm{H}} + k_{3t}k_{4t}\theta_{\mathrm{H}}^2]}{k_{3t}k_{4t}[k_{ct}\theta_{\mathrm{A}c} + k_{2t}(\mathrm{A})\theta_{\mathrm{MT}}][k_{ct}k_{-3c} + k_{ct}k_{4c}\theta_{\mathrm{H}} + k_{3c}k_{4c}\theta_{\mathrm{H}}^2]} \qquad (12)$$

At very low hydrogen pressure θ_H and θ_{MT} will be very small relative to the fraction of the surface occupied by hydrocarbon. Under these conditions, Eq. (12) simplifies to

$$d[cis]/d[trans] = k_{4c}K_{3c}/k_{4t}K_{ct}K_{3t} \quad (13)$$

where K_{3c} and K_{3t} are the equilibrium constants for

$$\mathrm{A(ads)} + \mathrm{H(ads)} \rightleftarrows \mathrm{HA(ads)}$$

and K_{ct} is the equilibrium constant for the interconversion of *cis*-A(ads) and *trans*-A(ads) on the surface.

At very high hydrogen pressures, on the other hand, the rates of the hydrogen addition steps become so large relative to the interconversion of *cis* and *trans* surface species that Eq. (6) simplifies to

$$d\theta_{Ac}/dt \cong 0 = k_{2c}[A]\theta_{MT} - k_{3c}\theta_{Ac}\theta_H \quad (14)$$

and Eq. (7) to

$$d\theta_{HAc}/dt \cong 0 = (k_{3c}\theta_{Ac} - k_{4c}\theta_{HAc})\theta_H \quad (15)$$

In combination with the equivalent expressions for the *trans* surface species, Eqs. (11), (14), and (15) lead to

$$d[cis]/d[trans] = k_{2c}/k_{2t} \quad (16)$$

for very high hydrogen pressures.

Thus the postulate that *cis*- and *trans*-1,2-diadsorbed alkanes can interconvert on the catalyst surface serves equally well to explain both the pressure-variable *cis/trans* product ratio observed in the hydrogenation of dialkylcyclohexenes and also the pressure-variable formation of *trans*-dialkylcyclohexanes from dialkylarenes. This postulate is consistent with the results of the competitive reactions reported here and appears to be required to explain the failure to observe more than traces of 1,2-dimethylcyclohexene in the course of hydrogenations of *o*-xylene which lead to very considerable amounts of *trans*-1,2-dimethylcyclohexane (*10*, *11*b).

The conditions implicit in Eqs. (14) and (15), hence those of Eq. (16), may not be attainable under practical laboratory procedures: therefore 100% *cis*-dialkylcyclohexanes from dialkylarenes is probably a limit which can only be approached. Also, some small amounts of tetrahydroarene intermediates clearly do desorb (*9–11*), and to the extent that they do, some still smaller amounts of *trans* products will be formed via this pathway. We regard desorbed tetrahydroarenes as incidental, however, and they will not make any significant contribution to the product isomer ratio when platinum catalysts are used. Even with ruthenium catalysts (*11*b) their effect will likely still be negligibly small.

It is incumbent to comment concerning some of the factors which influence the chemisorption of cycloalkenes on platinum surfaces. Three factors appear to be important: (a) the degree of substitution at the double bond: (b) internal strain: and (c) substituents at a distance from the double bond. The first is the largest (compare C_5, C_6, and C_7 in competition with their 1-methyl homologs, Tables 3 and 4). The last is much the smallest.

The preferential chemisorption of cyclopentene and cycloheptene, when they compete with cyclohexene, suggests that internal strain in the cycloalkene in solution relative to that of its 1,2-diadsorbed surface species is important. Thus *pseudo*-chair cyclohexene in solution proceeding to eclipsed 1,2-diadsorbed cyclohexane on the surface is less energetically favored than cyclopentene in solution (eclipsed) to 1,2-diadsorbed cyclopentane (also eclipsed) or flexible cycloheptene in solution to flexible 1,2-diadsorbed cycloheptane.

The effect on chemisorption of a substituent facing the catalyst surface at a distance from the double bond appears to be rather small (compare cyclohexene, 4-methyl- and 4,4-dimethylcyclohexene, Tables 3 and 4). Such a small effect intervening in the transition state to chemisorption can reasonably be expected to have an equally small counterpart effect upon the magnitude of K_{ct}, the equilibrium constant for the interconversion of *cis* and *trans* surface species. Hence the selectivity in the formation of *cis* vs. *trans* products using platinum catalysts might be expected to be small, as it is found to be (*2*).

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