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Hydrogenolysis of Saturated Hydrocarbons on a Nickel Catalyst

II. Selectivity of Hydrogenolytic Cleavage of Some Aliphatic and Alicyclic Hydrocarbons and Their Reactivity

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The hydrogenolysis of octane, decane, isooctane, neohexane, and some alicyclic hydrocarbons, like alkylcyclopentanes, alkylcycloheptanes, and dialkylcyclohexanes, in the gaseous phase on a nickel catalyst containing 8% (wt) Al_2O_3 was studied at 220°C under atmospheric pressure of hydrogen. In the hydrogenolysis of these hydrocarbons the predominant reaction was successive degradation to methane and a hydrocarbon containing one carbon atom less than the starting hydrocarbon.

In the case of isoparaffins, only the methyl groups bonded to secondary or tertiary carbon atoms and not those from quarternary carbon atoms were split off.

With dialkylcyclohexanes the alkyl groups were successively removed. The cleavage of the cyclohexane ring did not take place under the reaction conditions. The splitting of C–C bonds in the side chains of alkylcyclopentanes and alkylcycloheptanes was accompanied by hydrogenolytic opening of the ring.

The reactivity of branched-chain hydrocarbons was higher than that of corresponding hydrocarbons containing a straight chain. The high stability of the cyclohexane ring and the higher reactivity of alkylcyclohexanes than that of other alkylcyclanes is explained by the formation and electronic effect of a surface complex of quasiaromatic nature. The differences in the reactivity of hydrocarbons are discussed in terms of the participation of electronic and steric effects.

INTRODUCTION

In the study of hydrogenolysis of saturated aliphatic hydrocarbons attention has so far mainly been given to the splitting of ethane (*1–10*) on various metal catalysts such as nickel (*1, 2, 4, 6, 8–10*), platinum (*7*), iron (*5*), and cobalt (*3*). The growing extent of industrial catalytic hydrocracking has also initiated investigations of hydrogenolysis of individual hydrocarbons with straight (*11–17*) or branched chains (*11, 14, 17*) containing from six to nine carbon atoms in the molecule. In hitherto published work (*11–17*) it has been shown that hydrogenolytic splitting of carbon bonds proceeds for higher hydrocarbons fairly selectively only on nickel catalysts (*11, 13, 14, 17*) whereas catalysts containing platinum (*12, 14–16*), tungsten, and rhodium (*14*) also accelerate isomerization and other side reactions.

In the study of hydrogenolysis of alkyl- and dialkylcyclanes on metal catalysts attention has mainly been given to reactions of hydrocarbons containing three- to five-membered carbon rings (*18–25*). The splitting of alkylcyclanes with more than five carbon atoms in the ring, which takes place under more severe conditions and proceeds with lower selectivity, has so far been only rarely studied (*26–28*), and the interest has been centered mostly on the cleavage of the ring.

The present work concerns the hydrogenolysis of some saturated hydrocarbons on a nickel catalyst containing 92% (wt) nickel and only 8% (wt) aluminum oxide. In earlier work it has been found that this catalyst is very active and highly selective in the hydrogenolysis of alkylcyclohexanes (*29*), alkylcyclohexanones (*30*), and alkylphenols (*31, 32*). It was the purpose of the present work to determine the selectivity of cleavage of carbon bonds in aliphatic and in alicyclic hydrocarbons under very mild conditions, and also to determine the reactivity of these compounds.

EXPERIMENTAL

Materials. Octane, decane, neohexane (2,2-dimethylbutane), and isooctane (2,2,4-trimethylpentane) were commercial reagents denoted as chemically pure, supplied by Fluka A.G. The substances were refluxed prior to use in the presence of Raney nickel and then distilled on a laboratory column (60 TP). Pentane, hexane, heptane, nonane, 2-methylpentane, and neopentane used as testing substances for gas chromatography, were commercial reagents of Merck A.G., and Fluka A.G.; 2-methylhexane and 3-ethylhexane were obtained from Dr. M. Streibl (Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague), and 3-methyloctane and 3-ethylheptane were obtained from Dr. S. Hala (Department of Fuels, Institute of Chemical Technology, Prague).

Methylcyclopentane, ethylcyclopentane, methylcycloheptane, ethylcycloheptane were prepared by hydrogenation of the corresponding 1-alkylcyclenes. These substances were synthetized from cyclanones by the usual method (*33*). The values of the physical constants of the alkylcyclanes were in agreement with those given in the literature (*34, 35*).

Cyclopentane and cycloheptane were prepared by hydrogenation of cyclopentene and cycloheptene. The latter compounds were prepared by dehydration in the liquid phase of the corresponding cyclanoles with anhydrous $CuSO_4$.

All dialkylcyclohexanes (mixtures of stereoisomers) used in this work were obtained by hydrogenation of the corresponding dialkylbenzenes.

Pure *cis*- and *trans*-1,2-dimethylcyclohexanes were obtained by repeated distillation of a mixture of the two stereoisomers on an efficient laboratory column (70 TP). The values of the physical constants corresponded to those given in the literature (*33–36*).

The purity of all hydrocarbons used was checked by gas chromatography.

Hydrogen of the same source as in previous work (*29*) was used.

Catalyst. The nickel catalyst containing 8% (wt) of aluminum oxide was prepared by coprecipitation of the appropriate nitrates by an aqueous solution of potassium hydroxide. Details of the preparation have been given elsewhere (*29, 30, 37*). For kinetic measurements we took the fraction of mixed oxides of granular size from 0.5 to 1.0 mm, which was reduced for 4 hr by hydrogen at 350°C directly in the flow apparatus immediately before the experiment.

Apparatus and experimental procedure. The hydrogenolysis of aliphatic and alicyclic hydrocarbons was carried out in a flow apparatus of the usual type, in the manner described in earlier papers (*29, 30, 38*). Since the reactivity of the hydrocarbons was compared only on the basis of the initial reaction rate of hydrogenolysis, all experiments were carried out at 220°C with a partial pressure of hydrogen of 0.87 atm and 1 atm total pressure of both reactants, with a variable space velocity (F/W). Up to values of $x = 0.15$ the dependence of overall conversion on the reciprocal space velocity (W/F) was in all cases linear. The slope of the straight line obtained represents the magnitude of the initial reaction rate (r_0).

Analytical method. The liquid products of hydrogenolysis were analyzed by gas-liquid chromatography, analogously as described in the preceding paper (*29*). The temperature of the chromatographic column containing Apiezon L and dioctylsebacate coated on earthenware was from 40° to 140°C, depending on the molecular weights of the substances in the mixture to be analyzed.

Gaseous products of hydrogenolysis were analyzed by adsorption chromatography on aluminum oxide.

RESULTS AND DISCUSSION

Selectivity of Hydrogenolytic Cleavage

The experiments with aliphatic hydrocarbons have shown that hydrogenolysis on a nickel catalyst containing 8% (wt) of aluminum oxide is highly selective at 220°C. Under these conditions neither isomerization nor aromatization of the aliphatic hydrocarbons takes place. The liquid reaction products of hydrogenolysis (condensed in a bath of methanol and Dry Ice) consisted only of lower paraffins such as heptane, hexane, pentane, or neopentane and neohexane.

In the gaseous products of hydrogenolysis only methane was found. The direct decomposition of hydrocarbons to methane in the course of hydrogenolysis was very low and was estimated from the weight difference of the feed and the condensate, after correcting for losses due to the experimental procedure.

From the form of the dependence shown in Fig. 1 it is apparent that heptane is formed mostly as a primary product of octane hydrogenolysis, whereas the remaining hydrocarbons are formed predominantly by successive degradation. An analogous course of hydrogenolysis was found also with decane (see Fig. 2), the selectivity of splitting of the terminal C–C bond, however, being somewhat lower than in the hydrogenolysis of octane.

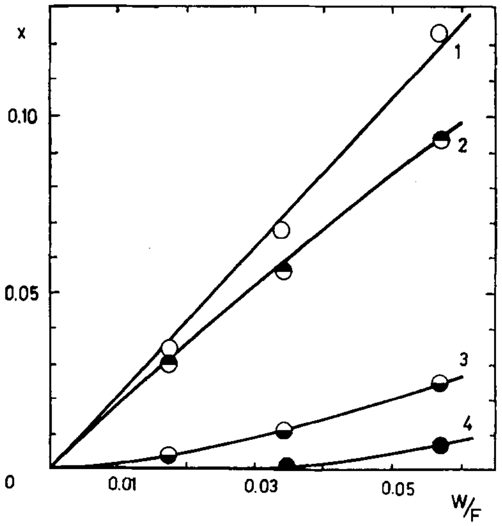


FIG. 1. Dependence of conversion (x) on reciprocal space velocity (W/F) in hydrogenolysis of octane on nickel catalyst at 220°C, 0.87 atm partial pressure of hydrogen, and total pressure 1 atm: 1, overall conversion; 2, conversion to heptane; 3, conversion to hexane; 4, conversion to pentane.

The successive degradation of n-paraffins in hydrogenolysis has already been observed by some authors (for example, *11*, *17*), but never with such a high selectivity as in the present case. In the hydrogenolytic cleavage of n-alkylcyclohexanes (*29*), n-alkylbenzenes (*39*), and n-alkylnaphthalenes (*40*) we have found earlier that predominantly successive degradation of the side chain takes place.

From the high content of heptane or nonane in the product of hydrogenolysis of octane or decane it may be deduced that the adsorbed reactants preferably form a structure which is bonded to the catalyst surface by the terminal methyl group and neighboring methylene group which on interaction with hydrogen yields methane and a hydrocarbon containing one carbon atom less than the starting paraffin.

It is interesting to note that on platinum catalysts (*12*, *14*, *16*), on which in addition

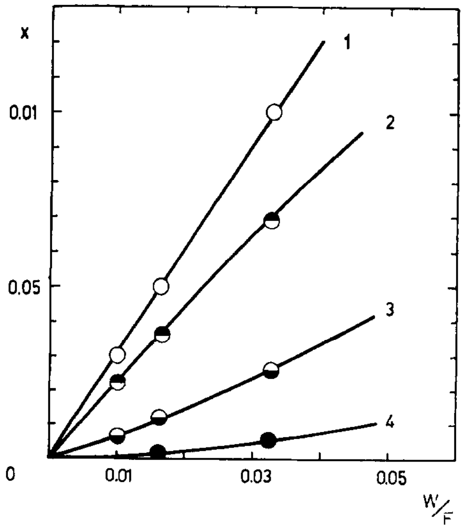
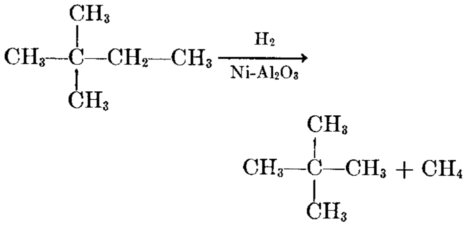


FIG. 2. Dependence of conversion (x) on reciprocal space velocity (W/F) in hydrogenolysis of decane under the same conditions as for Fig. 1: 1, overall conversion; 2, conversion to nonane; 3, conversion to octane; 4, conversion to heptane.

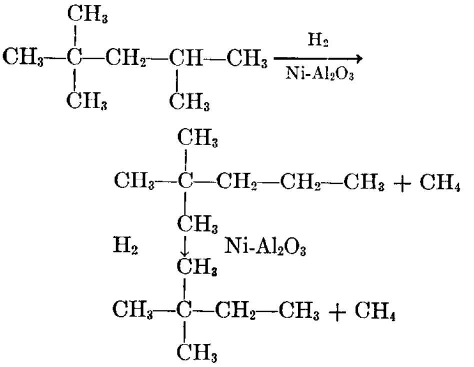
to hydrogenolysis of aliphatic hydrocarbons also their isomerization and aromatization take place to a considerable extent, probably other types of complexes are preferentially formed on the surface of the catalyst.

The selectivity of successive degradation of the hydrocarbon chain depends not only on the type of catalyst used but also on the reaction conditions, such as temperature, and pressure of hydrogen (compare with *11–17*).

In view of the fact that in the hydrogenolysis products of *n*-paraffins we have not found isomeric branched hydrocarbons, it is not possible to accept as an explanation for splitting on the catalyst used in the present work the opinions of Welker (*41*), who proposed an ionic mechanism for the hydrogenolysis of paraffins on metal bifunctional catalysts. From the results we have so far obtained in the study of hydrogenolysis of different types of hydrocarbons (*29, 39, 40*) it appears more likely that the carbonaceous surface fragments which are transitionally formed in the course of hydrogenolysis are of the nature of radicals and not of carbonium ions. This also follows from the fact that hydrogenolysis of neohexane and isooctane leads to products in which the neopentyl configuration is retained [Eqs. (1) and (2)].



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}CH_3} \xrightarrow[\mathrm{Ni\text{-}Al_2O_3}]{\mathrm{H_2}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_3} + \mathrm{CH_4} \tag{1}$$



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{CH}{-}CH_3} \xrightarrow[\mathrm{Ni\text{-}Al_2O_3}]{\mathrm{H_2}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}CH_2{-}CH_3} + \mathrm{CH_4} \tag{2}$$

$$\xrightarrow[\mathrm{Ni\text{-}Al_2O_3}]{\mathrm{H_2}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}CH_3} + \mathrm{CH_4}$$

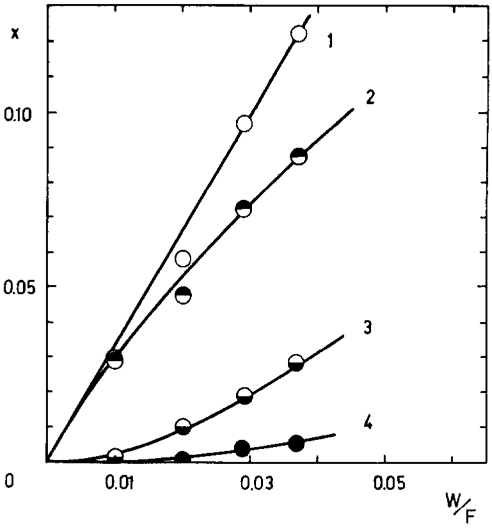
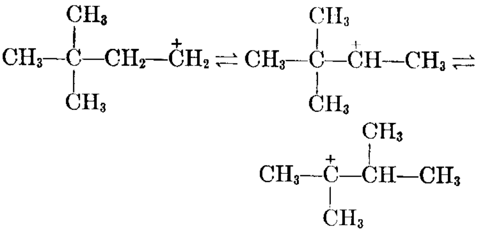


FIG. 3. Dependence of conversion (x) on reciprocal space velocity (W/F) in hydrogenolysis of 2,2,4-trimethylpentane (isooctane) under the same conditions as for Fig. 1: 1, overall conversion; 2, conversion to 2,2-dimethylpentane; 3, conversion to 2,2-dimethylbutane (neohexane); 4, conversion to 2,2-dimethylpropane (neopentane).

If the neohexyl carbonium ion were an intermediate in the hydrogenolysis of neohexane, then necessarily the migration of the methyl group would take place with the formation of the thermodynamically more stable carbonium ion [Eq. (3)]. The



$$\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\overset{+}{C}H_2} \rightleftharpoons \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\overset{+}{C}H{-}CH_3} \rightleftharpoons \mathrm{CH_3{-}\underset{CH_3}{\overset{+}{C}}{-}\overset{CH_3}{CH}{-}CH_3} \tag{3}$$

product of hydrogenolytic fission would be 2-methylbutane. From our results (Table 1) it is seen, however, that the only product is neopentane.

From Table 1 it further follows that also in the hydrogenolysis of isooctane the successive degradation of methyl groups from the isopropyl configuration took place. Methyl groups bonded to the quarternary carbon atom were not split off in hydrogenolysis [see Eq. (2)]. From the time course of the reaction (Fig. 2) it is apparent that 2,2-dimethylpentane and 2,2-

TABLE 1
PRODUCTS OF HYDROGENOLYSIS OF 2,2,4-TRIMETHYLPENTANE AND 2,2-DIMETHYLBUTANE[a]

Hydrocarbon	Overall conversion[b] (x)	Composition of liquid products (mole %)		
		2,2-Dimethylpentane	2,2-Dimethylbutane	2,2-Dimethylpropane
2,2,4-Trimethylpentane	0.05	88	12	—
2,2,4-Trimethylpentane	0.10	74	22	4
2,2-Dimethylbutane	0.10	—	—	99.5

[a] Reaction conditions: Ni–8% Al_2O_3 catalyst, 220°C, 0.87 atm partial pressure of hydrogen, total pressure 1 atm.

[b] Overall conversion represents the conversion of starting hydrocarbon to the sum of all hydrocarbons founded in the condensate.

dimethylbutane are formed from isooctane by successive reactions. A similar behavior has been observed in the hydrogenolysis of structurally analogous compounds such as isobutylcyclohexane and *sec*-butylcyclohexane (*29*).

As has been found recently (*29*), the hydrogenolysis of alkylcyclohexanes proceeds highly selectively: splitting of carbon bonds occurs only in the alkyl groups, and aliphatic hydrocarbons resulting from the cleavage of the cyclohexane ring are not formed even after long contact times. In the hydrogenolysis of alkylcyclanes with five- or seven-membered rings under the same conditions, however, the splitting of carbon bonds in the alkyl groups is accompanied by opening of the ring. Thus, for example, with ethylcyclopentane, as was to be excepted from the work of other authors (*18–25*), hydrogenolytic fission of the ring occurred to a larger extent than the cleavage of C–C bonds in the ethyl group. At a low overall conversion of ethylcyclopentane (see Table 2) the product of hydrogenolysis contains only substances formed by the primary cleavage of both the ring and side chain. A remarkable feature of this reaction is the considerable amount of heptane present in the product of hydrogenolysis. In hydrogenolysis of ethylcyclopentane on Pt (*21*), this hydrocarbon was formed to a lesser extent than 3-methylhexane and 3-ethylpentane. The hydrogenolytic splitting of methylcyclopentane on Pt (*20, 21*), Pt-Al_2O_3 (*23*), or on Ni (10 wt %)–Al_2O_3 (*42*) also proceeds predominantly on C–C bonds of the ring in the β-position to the carbon atom bearing the methyl group. The unusual cleavage in the α-position to the substituent of the cyclopentane ring is in disagreement with the findings of other authors and is probably due to the high content of nickel in the bifunctional catalyst. This hypothesis is supported by the fact that in the hydrogenolysis of *sec*-butylcyclohexane (*29*) on a catalyst containing 92% (wt) Ni and 8% (wt) Al_2O_3, the main product found was *n*-propylcyclohexane, while in the hydrogenolysis of *sec*-butylbenzene (*39*) on a catalyst composed of 50% (wt) of Ni and 50% (wt) of Al_2O_3 isopropylbenzene was formed predominantly. From this observation it can be deduced that the composition of the bifunctional nickel catalyst has a certain influence on the hydrogenolytic splitting of C–C bonds in the β- or α-position to the branching of the carbon chain.

TABLE 2
PRODUCTS OF HYDROGENOLYTIC FISSION OF ETHYLCYCLOPENTANE[a]

Overall conversion (x)	Product of side-chain cleavage (mole %) Methylcyclopentane	Products of ring opening (mole %)	
		Heptane	3-Methylhexane and 3-ethylpentane
0.06	18.3	68.7	13.1
0.09	16.0	61.5	22.5

[a] Reaction conditions given in Table 1.

With both methyl- and ethylcycloheptane (see Table 3) opening of the ring occurred to a lesser extent, and products of splitting of C–C bonds in alkyl groups ac-

TABLE 3

Products of Hydrogenolytic Fission of Methylcycloheptane and Ethylcycloheptane[a]

	Composition of liquid products (mole %)	
	$CH_3—C_7H_{13}$[b]	$C_2H_5—C_7H_{13}$[c]
Products of side-chain cleavage		
Methylcycloheptane	—	40.0
Cycloheptane	80.8	28.3
Products of ring opening		
2-Methylheptane	8.8	6.5
2-Ethylhexane	2.6	—
Octane	3.1	—
2-Methylhexane	0.9	—
2-Ethylpentane	0.5	6.9
Heptane	3.3	18.3

[a] Reaction conditions given in Table 1.

[b] Overall conversion $x = 0.19$.

[c] $x = 0.10$.

counted for more than 68% (mole) of the reacted fraction even at rather high degrees of conversion.

As is apparent from Table 4, however, in the series of some dialkylcyclohexanes, similarly as with some alkylcyclohexanes (*29*), hydrogenolytic splitting was highly selective. So, for example, in the splitting of 4-methyl-1-isopropylcyclohexane, the same ratio of products of successive degradation was found as with isopropylcyclohexane itself.

With methylethylcyclohexanes, hydrogenolysis resulted only in splitting of C–C bonds in the ethyl group, because the methyl group bonded to the cyclohexane ring is substantially less reactive (*29*).

Also in the hydrogenolysis of dialkylcyclohexanes, only methylcyclohexane was formed at longer contact times. This proves that hydrodealkylation is a consecutive reaction, which is due to the fact that when adsorption on the surface takes place, hydrogenolytic cleavage can proceed only on one reaction center in the hydrocarbon molecule.

In the course of hydrogenolysis of dialkylcyclohexanes shifts of alkyl groups over the cyclohexane ring have not been observed. However, equilibrium transformations of stereoisomers of the starting hydrocarbons or products of hydrogenolysis proceeded very rapidly. For this reason we used for most cases of hydrogenolysis a mixture of stereoisomeric dialkylcyclohexanes. Only in the case of 1,2-dimethylcyclohexane was the reaction carried out with pure stereoisomers which, however, we did not succeed in demethylating under the chosen conditions; the reaction products were always an equilibrium mixture of stereoisomers.

The results given in Table 4 indicate the considerable stability of the cyclohexane ring, which also follows from the work of Slovokhotova *et al.* (*43*, *44*). Since higher hydrocarbons, such as cyclononane, cyclodecane, and cycloundecane, in which the ring strain is of significance, are readily hydrogenolyzed on nickel catalysts already at 200°C (*26*, *27*), it is hardly pos-

TABLE 4

Products of Hydrogenolytic Fission of Dialkylcyclohexanes[a]

Hydrocarbon	Overall conversion (x)	Composition of liquid products (mole %)				
		4-Methyl-1-ethylcyclohexane	Methylcyclohexane	Dimethylcyclohexanes		
				1,2-	1,3-	1,4-
4-Methyl-1-isopropylcyclohexane	0.09	87.0	—	—	—	13.0
2-Methyl-1-ethylcyclohexane	0.07	—	—	100	—	—
3-Methyl-1-ethylcyclohexane	0.20	—	—	—	100	—
4-Methyl-1-ethylcyclohexane	0.17	—	—	—	—	100
1,3-Dimethylcyclohexane	0.03	—	100	—	—	—
1,4-Dimethylcyclohexane	0.06	—	100	—	—	—

[a] Reaction conditions given in Table 1.

sible to explain the exceptional stability of cyclohexane, as compared with that of other cyclanes, by the small ring strain of the six-membered ring. It appears more likely that the stability of the cyclohexane ring under conditions of hydrogenolysis can be ascribed to the specific mode of its adsorption on metal catalysts.

The Effect of Structure of Hydrocarbons on Their Reactivity

From the results given in Table 5, it is apparent that the reactivity of decane is higher than that of octane. This is probably due also to the fact that the initial reaction rate includes, in addition to the rate constant, also the adsorption coefficients of hydrocarbons, the values of which increase with the molecular weight. The reactivity of neohexane, for which hydrogenolysis affects only the terminal methyl group of the ethyl radical bonded to the quarternary carbon atom, is lower than that of *n*-paraffins. The decrease in the reactivity of neohexane can be explained on the basis of the steric hindrance of the split C–C bond by the neighboring tertiary butyl group.

The most reactive of the investigated aliphatic hydrocarbons was found to be isooctane, for which the primary step was the cleavage of one methyl group from the isopropyl configuration. The higher reactivity of isooctane as compared with that of *n*-octane is in agreement with what has been found earlier in the splitting of some alkylcyclohexanes with straight or branched side chains (*29*).

It is interesting, however, that other authors (*11*, *17*) who have studied hydrogenolysis of some isoparaffins on nickel catalysts containing only 5–15% (wt) of nickel and 85–95% (wt) of alumina or silica, have found that the reactivity of straight-chain hydrocarbons is higher than that of hydrocarbons with branched chains. It may therefore be deduced that the differing reactivity of isoparaffins is due to the differences in the adsorptivities of these hydrocarbons on catalysts containing 85–95% (wt) of Al_2O_3 or only 8–10% (wt) of Al_2O_3. This is also in agreement with the observation that alkylaromatic hydrocarbons with straight side chains were more reactive than the isomeric hydrocarbons with branched side chains on nickel catalysts containing 50–60% (wt) of alumina.

TABLE 5
Initial Reaction Rate of Hydrogenolysis of Some Aliphatic Hydrocarbons[a]

Hydrocarbon	r_0 (mole/hr kg cat)
Octane	2.1
Decane	3.0
2,2,4-Trimethylpentane	3.3
2,2-Dimethylbutane	1.6

[a] Reaction conditions given in Table 1.

TABLE 6
Initial Reaction Rates of Hydrogenolysis of Some Alkylcyclanes[a]

Hydrocarbon	r_0 (mole/hr kg cat) Overall	Cleavage of alkyl group	Opening of ring
Ethylcyclopentane	3.5	0.6	2.9
Ethylcyclohexane[b]	12.0	12.0	—
Ethylcycloheptane	1.7	1.2	0.5
Methylcyclohexane[b]	0.1	0.1	—
Methylcycloheptane	2.7	2.2	0.5

[a] Reaction conditions given in Table 1.
[b] See ref. (*29*).

The effect of the ring size has also been studied for some alkylcyclanes from the viewpoint of how it affects the rate of hydrogenolytic cleavage of C–C bonds in the side chain. From the results given in Table 6 the large difference in reactivities of ethylcyclohexane or ethylcycloheptane is apparent. It is not probable that this difference can be accounted for by the induction effect of the cyclohexyl group itself, which differs only little from that of the remaining cycloalkyl groups, and it is apparently due to the electronic action of the surface complex formed by the cyclohexane ring.

In previous work on hydrogenolysis of hydrocarbons (*29*, *39*, *40*) it has been found that electronegative substituents bonded to the aliphatic C–C bond accelerate its splitting. From this it can be concluded that the nature of the assumed surface complex of the cyclohexane ring approximates to that of a quasiaromatic structure, and by its electronegativity it increases the reactivity of C–C bonds in the side chain of alkylcyclohexanes. This concept can also serve to explain some other features of hydrogenolysis of alkylcyclanes. So, for example, for methylcyclohexane we may suppose that the splitting off of the methyl group from the cyclohexane ring will be retarded by the effect of the quasiaromatic nature of the surface complex, because of the mesomeric stabilization of the methyl group. On the other hand, for methylcycloheptane, which cannot form a surface complex of quasiaromatic nature and for which mesomeric stabilization is also out of the question, the methyl group is split off at a higher rate, as is seen from the data in Table 7.

The concept of the quasiaromatic nature of the cyclohexane surface complex is also supported by the results of hydrogenolysis of dialkylcyclohexanes. For example, the lower reactivity of 4-methyl-1-isopropylcyclohexane and methylethylcyclohexanes as compared with hydrocarbons not containing methyl groups (Table 7) can probably be explained by the electronic effect of the methyl group, because the transfer of an electronic charge to a distant reaction center is facilitated by a quasiaromatic structure of the adsorbed species.

TABLE 7
INITIAL REACTION RATES OF HYDROGENOLYSIS OF SOME DIALKYLCYCLOHEXANES[a]

Hydrocarbon	r_0 (mole/hr kg cat)
4-Methyl-1-isopropylcyclohexane[b]	7.0
Isopropylcyclohexane[c]	13.0
2-Methyl-1-ethylcyclohexane[b]	0.3
3-Methyl-1-ethylcyclohexane[b]	2.3
4-Methyl-1-ethylcyclohexane[b]	4.4
Ethylcyclohexane[c]	12.0
1,2-Dimethylcyclohexane (*cis* and *trans*)	—
1,3-Dimethylcyclohexane[b]	0.2
1,4-Dimethylcyclohexane[b]	0.6
Methylcyclohexane[c]	0.1

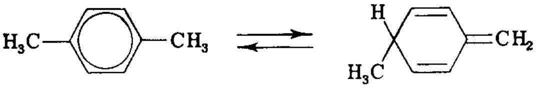
[a] Reaction conditions given in Table 1.

[b] Mixture of stereoisomers.

[c] See ref. (*12*).

It cannot be excluded that in addition to electronic effects also steric effects caused by the direct shielding of the reaction center by the methyl group, especially in the hydrogenolysis of 2-substituted alkylcyclohexanes, play some role.

From the values given in Table 7 it is also apparent that 1,4- and 1,3-dimethylcyclohexanes are more reactive than methylcyclohexane. The probable explanation for this is that, because of mesomery, one methyl group in the quasiaromatic surface complex is stabilized and the other one is more easily split off, as is indicated by Eq. (4).



(4)

The successive decrease in reactivity from 1,4-dimethylcyclohexanes to 1,2-dimethylcyclohexanes is probably also due to a combination of electronic and steric effects on the reaction center, as in the case of methylcyclohexanes.

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