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The Mechanisms of Hydrogenolysis and Isomerization of Hydrocarbons on Metals

I. Hydrogenolysis of Cyclic Hydrocarbons

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The hydrogenolysis of methylcyclobutane and various substituted cyclobutanes and cyclopentanes has been studied on metal films and on the corresponding metal-on-alumina catalysts.

The product distribution on metal films depends on the metal, the reaction temperature, and the hydrogen pressure; on supported catalysts, it depends on the concentration of the metal on the carrier.

At high temperature, on platinum and palladium films and on the supported catalysts with low metal content, a typical distribution is obtained with any hydrocarbons, corresponding to an equal chance to break the different cyclic bonds of the molecules. π-Allylic triadsorbed species are thought to be responsible for this type of hydrogenolysis.

On 10% platinum on alumina or platinum film, at low temperature, and on nickel, only the disecondary CH_2–CH_2 cyclic bonds of cyclobutanes and cyclopentanes are broken. $\alpha,\alpha,\beta,\beta$-Tetraadsorbed species could be associated with this selective hydrogenolysis.

The analysis of the product distributions obtained from methylcyclopentane on platinum-alumina catalysts and the hydrogen pressure dependency of the hydrogenolysis of methylcyclobutane on platinum films suggest that another mechanism takes place on this metal.

The similarity of the product distributions on films and supported catalysts shows that the carrier does not play a catalytic role in the reaction.

The difference of the product distributions in the hydrogenolysis of *cis*- and *trans*-dimethylcyclopropanes is also discussed.

INTRODUCTION

The hydrogenolysis of cyclic hydrocarbons was first investigated by Kazanskii and coworkers on platinum-charcoal (*1*). They showed that the cyclic bonds were selectively opened and gave the product distributions for a number of substituted cyclopentanes (*2*, *3*) and cyclobutanes (*4*).

The variations with the experimental conditions of the product distributions were investigated in the hydrogenolysis of methylcyclopentane on different platinum-alumina catalysts, under pressure, and under such conditions that no further isomerization or extensive cracking of the hexanes took place (*5*). It was shown that the distributions depended mostly on the concentration of the platinum on the alumina: On a catalyst with a high metal content (6% platinum and more on alumina), a selective hydrogenolysis of the CH_2–CH_2 disecondary bonds occurred; on a catalyst with a low metal content (0.6% and lower), the five cyclic bonds were almost equally opened; catalysts with 0.6–6% platinum on alumina showed an intermediate behavior.

This effect was first interpreted by a high dispersion of the platinum on alumina in catalysts with low metal contents (*6*). This interpretation had some physical support, since Spenadel and Boudart have shown, by adsorption measurement, an almost atomic dispersion of the metal in such catalysts (*7*). Since then, several authors have assumed such a dispersion to interpret their results (*8*).

Newham, reviewing the results on hydrogenolysis (*9*), suggested an alternative explanation based on the acidity of the alumina. Some evidence against such an effect of the alumina in these conditions was first summarized in a preliminary note in this Journal (*10*) and will be developed further.

However, in order to investigate if the alumina does or does not play a role in hydrogenolysis, a parallel study of the reaction on platinum-alumina and on platinum films seemed desirable.

A further reason for this study was to determine, if possible, the mechanism of the hydrogenolysis of cyclic hydrocarbons.

Most of the experiments were done with methylcyclobutane instead of methylcyclopentane, because the lower reaction temperature for this compound makes easier a kinetic study on evaporated films, and nullifies the side reactions, such as isomerization and cracking of the alkanes, on supported catalysts.

EXPERIMENTAL

Apparatus. The reactions on evaporated films were studied in a static system; the reaction vessel was connected to the source of a mass spectrometer, as described by Kemball (*11*), so that the kinetics of the reaction could be followed without interruption. The standard reaction mixture was 5 mm of hydrocarbon and 60 mm of hydrogen in a reaction vessel of 200 ml.

The reaction on supported catalysts was investigated using a gas chromatograph connected with an all-glass microreactor (diameter 4 mm); the hydrogen was used as a reactant and a carrier gas in chromatography, after purification on a platinum catalyst. Different contact times were obtained by varying the amount of catalyst in the microreactor (0.5 to 2 mg).

Several doses of methylcyclopentane or methylcyclobutane were successively passed on the same catalyst to test the reproducibility of the experiments. When a 10% platinum-alumina catalyst was used, at any temperature, or a dispersed catalyst (less than 2% platinum on alumina) at temperatures below 280°C, the over-all conversion was reproducible within ±10% and the product distribution within ±3%. Thus the same amount of catalyst could be used for a large number of runs without any modification.

On the other hand, a dispersed catalyst, when brought to a temperature of 280°C and above, was slowly deactivated, and the product distribution was modified. This modification of the catalyst occurs even in the absence of any reaction and will be examined in the following sections.

Two milligrams of methylcyclobutane and 4 mg of methylcyclopentane were used in each run. It was also tested that the product distribution was not altered when the amount of a dose was modified by ±50%.

Catalysts. The methods of preparation of the films have been described previously (*11*); "Specpure" samples of metals were obtained from Johnson-Matthey.

The method of preparation of the platinum-on-alumina catalysts has been described by Pines, Olberg, and Ipatieff (*12*); the temperature of the reduction of the platinum chloride was kept below 200°C. The other supported catalysts were prepared following a similar procedure.

Pure grade platinum and palladium chlorides were obtained from Caplain St-André; γ alumina was obtained from Woelm.

Materials. Pure samples of methylcyclobutane were prepared by hydrogenation on Raney nickel of methylene cyclobutane. The use of pressure and moderate temperatures (60°) permits the hydrogenation of the spiropentane and the isopentenes present as impurities, to neopentane and isopentane respectively, without any hydrogenolysis of the four-membered ring.

1,2-Dimethylcyclopentanes were prepared from methylcyclopentanone by condensation with methyl magnesium bromide, dehydration of the tertiary alcohol, and hydrogenation of the cycloolefins.

1,2-Dimethylcyclopropanes were prepared from the 2,4-dibromopentane, according to

Bartleson *et al.* (*13*) and the *cis* and *trans* isomers separated by gas chromatography. Chromatography on a benzonitrile–silver nitrate column showed that no olefin impurity was present in the hydrocarbons.

1,2-Dimethylcyclobutane was prepared from 1-methylene-2-methylcyclobutane in a microhydrogenator placed in the reaction flow line just before the microreactor.

Every hydrocarbon was purified by gas chromatography before use. Cylinder hydrogen used in the static system was purified by diffusion through a palladium thimble.

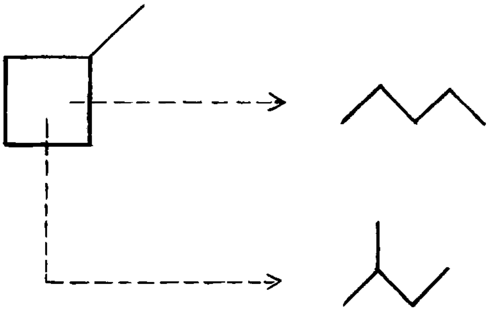
Mass spectrometric analysis. Ions at masses 57, 72, and 70 were used for the analysis of methylcyclobutane, isopentane, and pentane. The electron acceleration voltage was 25 V. To avoid errors due to a change in fragmentation, the mass spectra of the three pure hydrocarbons were recorded before any experiment.

Gas chromatography. Silicone oil columns were used for both analytical and preparative purposes. Methylcyclobutane, methylcyclopentane, dimethylcyclopropanes, and dimethylcyclopentanes were easily separated from their hydrogenolysis products at room temperature. *cis*-Dimethylcyclobutane and the reaction products, 3-methylpentane, 2,3-dimethylbutane, and *n*-hexane were also resolved in these conditions. But *trans*-dimethylcyclobutane and 2,3-dimethylbutane were only partially resolved, even at a column temperature as low as −20°C. Thus, in hydrogenolysis of dimethylcyclobutane, an accurate analysis of 2,3-dimethylbutane is only possible for a total conversion.

RESULTS AND INTERPRETATION

I. Hydrogenolysis of Methylcyclobutane on Supported Catalysts

The hydrogenolysis of methylcyclobutane on supported platinum and palladium catalysts only gave isopentane and pentane as reaction products, in a large range of temperature. The selectivity factor *r*, the ratio of isopentane to *n*-pentane, and the conversion α, the ratio of pentanes to total products, were always considered as described in the following sections.



A. Platinum-Alumina

Variation of the selectivity factor with the conversion. The plots $r = f\ (\alpha)$ represented in Fig. 1 for different platinum-on-alumina catalysts, show that the selectivity factor *r* does not vary much with the conversion at a given temperature, but depends mostly on the percentage of platinum in the catalyst; the hydrogenolysis on a 10% platinum-alumina catalyst (concentrated catalyst) is far more selective than the hydrogenolysis on catalysts of lower metal content (dispersed catalyst).

The variation of *r* with conversion on a 10% platinum-alumina catalyst, although slight, was too substantial to be due to the experimental errors.

Variation of *r* with the temperature. The selectivity factor *r* was determined for the same contact time over a large range of temperature where neither cracking nor iomerization of the reaction products tooks place (130–280°C). Characteristic $r = g(T)$ plots are thus obtained for the different catalysts and reported in Fig. 2. Most of these plots correspond to a conversion higher than 90%. When they do not, and in the case of à 10% platinum-alumina catalyst only, the values of α are as shown in the figure.

When the reaction took place on a concentrated catalyst, *r* did not vary much with the temperature; the apparent slight variation of *r* with the temperature only corresponded to the variation with the conversion. However, on dispersed catalysts, a large decrease of the selectivity factor was observed when the temperature was increased.

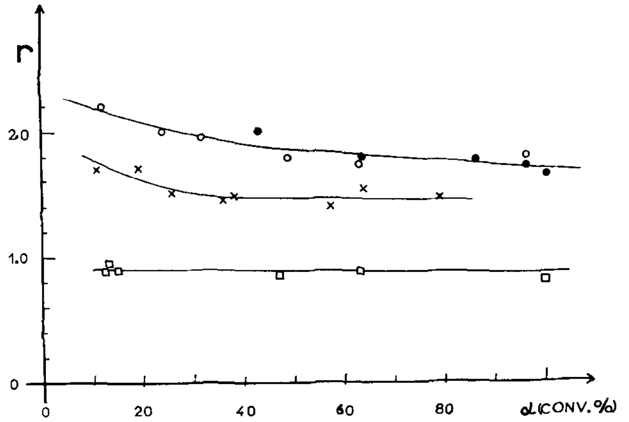


FIG. 1. Selectivity factor, $r = f$ (α) plots for different platinum-alumina catalysts: 10% Pt on alumina at 146°C, ○, and at 164°C, ●; 1% Pt on alumina at 158°C, ×; 0.2% Pt on alumina at 228°C, □.

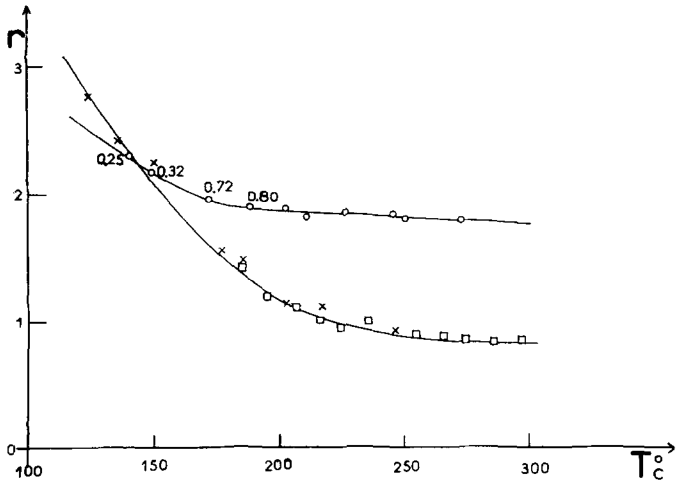


FIG. 2. Selectivity factor; variation of r with the temperature: 10% Pt on alumina, ○; 0.5% Pt on alumina, ×; 0.2% Pt on alumina, □.

Effect of a thermal treatment of the catalyst. When a dispersed catalyst had been brought to a temperature of 400°C, the selectivity factor was decreased. On a 0.2% platinum-alumina catalyst heated at 400°C, r remained constant and equal to 0.9 at any temperature. In Fig. 3, the properties of a 1% platinum-alumina catalyst, after treatment at 280° and then at 400° are represented by their $r = g(T)$ plots. In contrast, there was no change for concentrated platinum-alumina catalyst, after treatment at 400°C in hydrogen.

B. Palladium-Alumina

The hydrogenolysis of methylcyclobutane was slower on palladium than on platinum and was studied at higher temperatures, between 200° and 300°C. The same effect of the concentration of the metal on the carrier, and the same decrease of the selectivity factor with an increase in temperature were observed, as can be seen from the plots in Fig. 4. However, the "dispersion effect" was smaller in the case of palladium-alumina catalysts, and the selectivity factor r on a 10% palladium-alumina catalyst was only

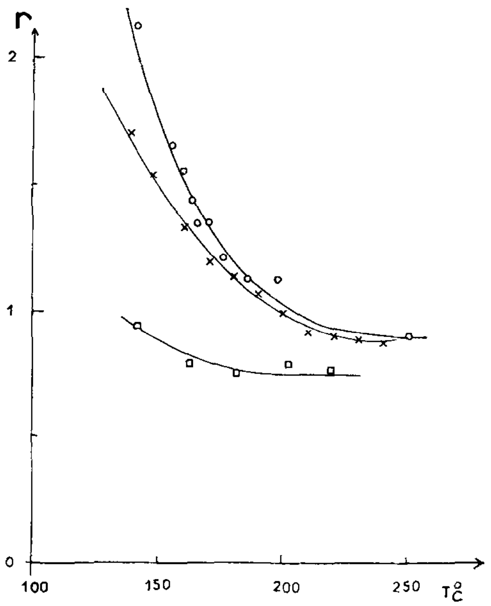


Fig. 3. Effect of the thermal treatment of a 1% platinum-alumina catalyst on the product distributions: catalyst heated at 200°C, ○; heated at 280°C for 14 hr, ×; heated at 400°C for 40 hr, □.

1.6 at 260°C, compared with 1.85 on the corresponding platinum catalyst at the same temperature.

C. Reactions of Methylcyclobutane and Methylenecyclobutane on Alumina

Methylcyclobutane and methylenecyclobutane were introduced on alumina in the same flow system as that used for the study of hydrogenolysis. It was first tested that methylcyclobutane was not reacting at temperatures below 400°C.

Up to 230°C on alumina, methylenecyclobutane was converted to a hydrocarbon which was hydrogenated on platinum-pumice at 100°C to methylcyclobutane; thus only double-bond shift took place in these conditions. At temperatures higher than 230°C, an isomerization with the rupture of the ring took place; the diene obtained was hydrogenated to isopentane and thus was probably isoprene. However, the extent of reaction was only 25% at 270°C.

Under the experimental conditions for which hydrogenolysis has been studied, the alumina cannot be taken as playing a major role in the reaction of ring opening.

D. Platinum and Palladium on Pumice

On a 10% platinum-pumice catalyst, the selectivity factor was almost constant and equal to 2.2 ± 0.2, between 200° and 350°C.

On a 10% palladium-pumice catalyst, *r* steadily decreased from 2.45 at 310°C to 1.6 at 390°C.

No opening of the ring was observed up to 350° when either methylcyclobutane or methylenecyclobutane was passed over pumice.

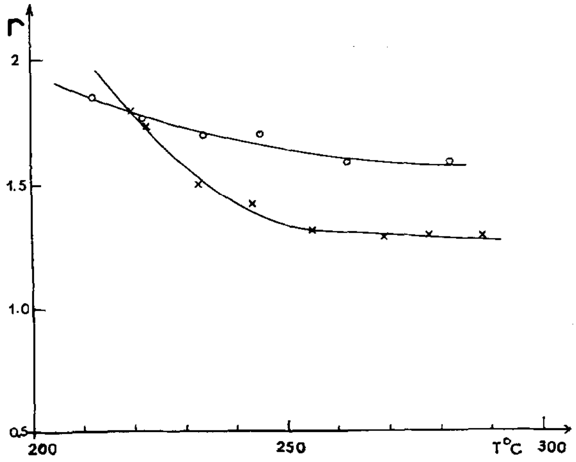


Fig. 4. **Hydrogenolysis on palladium-alumina catalysts: 10% palladium on alumina, ○; 1% palladium on alumina, ×.**

TABLE 1
VALUES OF THE SELECTIVITY FACTOR IN THE HYDROGENOLYSIS OF METHYLCYCLOBUTANE AT VARIOUS TEMPERATURES AND HYDROGEN PRESSURES ON METAL FILMS

Catalyst	H_2 pressure							
Platinum	16 mm	T°C:	50					
		r:	0.95					
	55 mm	T°C:	51	72	82	105	120	150
		r:	2.06	1.80	1.66	1.44	1.30	1.0
	160 mm	T°C:	50	100	130			
		r:	4.4	1.57	0.95			
Nickel	55 mm	T°C:	85	100	120	145	200	
		r:	9.9	9.0	8.0	6.4	3.9	
Palladium	55 mm	T°C:	130	142	155	172	207	
		r:	2.62	2.34	1.94	1.53	1.22	

II. Hydrogenolysis of Methylcyclobutane on Evaporated Metal Films

Isopentane and *n*-pentane were obtained in the hydrogenolysis of methylcyclobutane, as the only reaction products on platinum and palladium films and the main ones on nickel film.

Selectivity factor. The selectivity factor only depended on the catalyst and on the temperature; *r* was always independent of the conversion. Table 1 clearly shows the variations of *r* according to temperature on platinum, palladium, and nickel: In each case, increasing the temperature decreased the selectivity factor. Whereas on platinum and palladium, *r* varied between 2.3 and 1, on nickel the hydrogenolysis was far more selective; *r* was never found to be smaller than 3.

Kinetic data. To determine the reaction order versus hydrocarbon, the logarithm of the concentration of methylcyclobutane was plotted against time in a number of experiments; straight lines were obtained in every case (Fig. 5), which shows first order kinetics. Activation energies and frequency

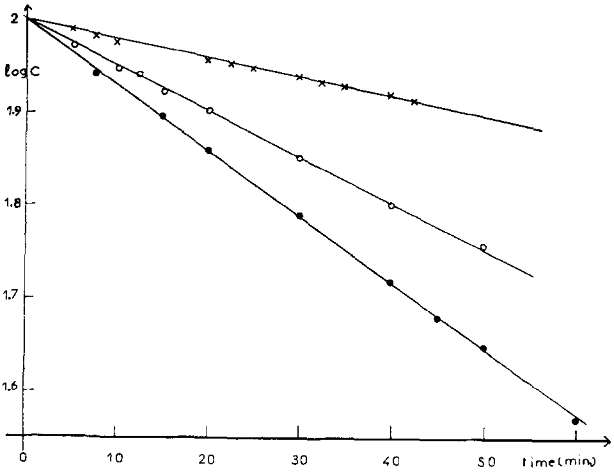


FIG. 5. Hydrogenolysis of methylcyclobutane on metal films; results plotted according to a first order kinetic law: palladium at 155°C, ×; nickel at 145°C, ○; platinum at 72°C, ●; *C*; concentration of methylcyclobutane.

factors are reported in Table 2 for nickel, palladium, and platinum.

TABLE 2
ACTIVATION ENERGIES AND FREQUENCY FACTORS OF THE HYDROGENOLYSIS OF METHYLCYCLOBUTANE ON DIFFERENT METAL FILMS

Metal	$\log_{10} A^a$	E (kcal/mole)	Temp. (°C) for rate = 10^{-2} min^{-1}
Platinum	23.7	16.5	70°
Palladium	23.3	19.5	170°
Nickel	17.5	8	136°

[a] A is expressed in reacted molecules per minute, per 10 mg of platinum or nickel, per 100 cm² apparent area of palladium.

Hydrogen pressure dependency. The hydrogen pressure dependency of both reaction rates and selectivity factors varied with the temperature, on platinum films. The reaction order versus hydrogen was always negative, but varied from −1.7 at 50° to −2.0 at 100° and to −1.15 at 130°C. When the hydrogen pressure was multiplied by 3, the selectivity factor, as shown in Table 1, increased at 50°C, did not change much at 100°, and decreased at 130°C.

This hydrogen pressure dependency of the selectivity factor is seen clearly in Fig. 6 where r is plotted as a function of the temperature for various pressures of hydrogen.

Self-poisoning and extensive cracking. On nickel film, an extensive cracking to hydrocarbons of lower molecular weight accompanied the simple hydrogenolysis of the ring. In Table 3 the rates of formation at 180°C of butanes, propane, ethane, and methane are reported and compared to the rate of hydrogenolysis of the ring.

At 190°C, the hydrocarbons in the range C_1–C_4 only represented 2% of the reaction products on platinum films, and on palladium these hydrocarbons could not be detected.

After presorption of methylcyclobutane at 180°C for 30 min, a platinum film became inactive even at 200°C for the hydrogenolysis. When the poisoned film was brought to a temperature of 290°C in hydrogen, an evolution of methane was observed.

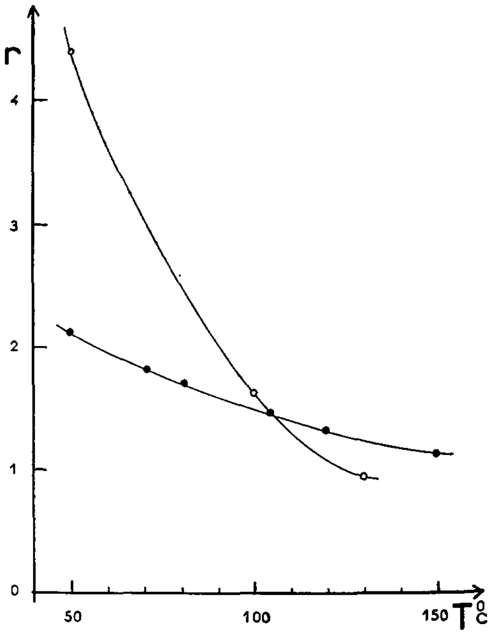


FIG. 6. Hydrogenolysis of methylcyclobutane on platinum films; hydrogen pressure dependency of the selectivity factor: 55 Torr hydrogen, ●; 160 Torr hydrogen, ○.

III. Hydrogenolysis of Methylcyclopentane on Platinum-Alumina Catalysts

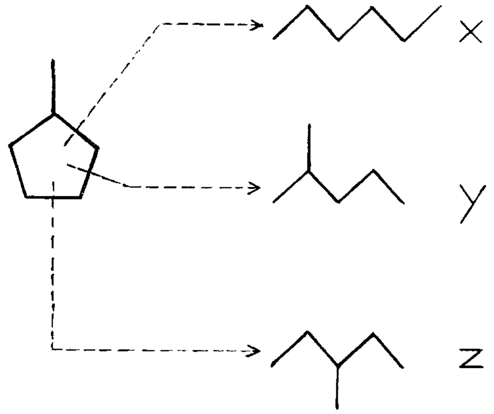
Three hydrocarbons, n-hexane, 2-methylpentane, and 3-methylpentane were formed in the hydrogenolysis of methylcyclopentane. On a given catalyst, the product distributions widely varied with temperature and were independent of the conversion, when no isomerization or cracking of the primary products took place. As the reaction has been extensively studied previously (*5*, *6*) it will be examined in this section only to see if the observed product distribution can be considered as a combination of two

TABLE 3
RATES OF EXTENSIVE CRACKING OF METHYLCYCLOBUTANE ON NICKEL FILMS AT 180°C

Products:	Methane	Ethane	Propane	Butanes	n-Pentane	Isopentane
Rates: (%/min)	1.95	0.40	0.53	0.82	1.85	7.36

limit distributions or of more than two.

It was easily checked that any distribution x, y, z, observed in the hydrogenolysis of methylcyclopentane on a 10% platinum-alumina catalyst at 230–310°C, could be expressed as a linear combination of two distributions.



If the distributions 1 (x_1, y_1, z_1) and 2 (x_2, y_2, z_2) obtained at the extreme temperatures, are chosen as limit distributions:

$$x = c_1x_1 + c_2x_2 \quad \text{(1a)}$$

$$y = c_1y_1 + c_2y_2 \quad \text{(1b)}$$

$$z = c_1z_1 + c_2z_2 \quad \text{(1c)}$$

provided $x + y + z = x_i + y_i + z_i$, $c_1 + c_2 = 1$; c_1 and c_2 $(= 1 - c_1)$ can be calculated from Eq. (1a) for each experiment. Using these values of c_1 and c_2 in (1b) and (1c), calculated values of y and z can be obtained and compared to the observed values.

In Table 4, x, y, z, c_1, and the differences Δy and Δz between calculated and observed values of y and z are given as examples for some experiments; Δy and Δz are very small.

The distribution given in the sixth line of the table was obtained on a 0.2% platinum-alumina catalyst in a large range of temperature; it is not a combination of 1 and 2.

The product distributions obtained on a 1% platinum-alumina catalyst were similarly treated: Δy and Δz were then always much larger than in the preceding case. Thus the observed distributions are not combinations of two independent distributions 1′ and 2′, but must be expressed as combinations of more than two distributions.

IV. Hydrogenolysis of 1,2-Dimethylcycloalkanes

A. Hydrogenolysis of 1,2-Dimethylcyclobutane on Platinum-Alumina Catalysts

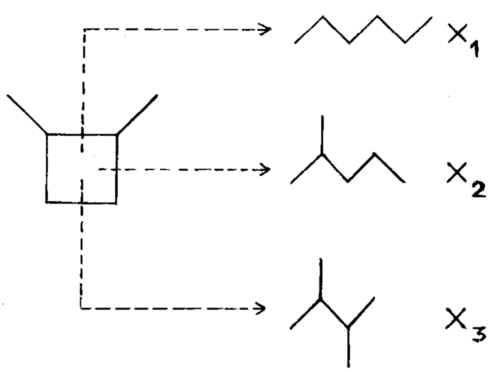
Three reaction products, 2,3-dimethylbutane, 3-methylpentane, and *n*-hexane were obtained from 1,2-dimethylcyclobutane. The different ratios between the reac-

TABLE 4

Product Distributions in the Hydrogenolysis of Methylcyclopentane on Various Platinum-Alumina Catalysts[a]

Catalyst	T(°C)	Run No.	x	y	z	c_1	Δy	Δz
$Pt-Al_2O_3$ 10%	316	1	11.1	60.9	28.0	100	—	—
	233	2	0	78.3	21.7	0	—	—
	300	3	8.3	64.7	26.9	75.3	0.4	−0.5
	289	4	5.7	69.1	25.1	51.8	0.18	−0.17
	275	5	4.15	71.7	24.1	37.5	0.05	0.05
$Pt-Al_2O_3$ 0.2%	250—310	6	37.6	41.7	20.7	—	—	—
$Pt-Al_2O_3$ 1%	203	1′	15.0	63.2	21.8	100	—	—
	301	2′	24.1	50.4	25.5	0	—	—
	210	3′	16.6	65.9	17.5	82.0	−5.1	5.1
	224	4′	17.3	64.0	18.7	74.3	−4.0	4.0
	241	5′	19.3	61.2	19.5	52.7	−4.1	4.0

[a] x, y, z are the concentrations of *n*-hexane, 2-methylpentane, and 3-methylpentane in the reaction products, respectively. Δy = y calculated − y observed.



tion products are given in Table 5 for 10% and 0.2% platinum-alumina catalysts, between 160° and 260°C. The upper limit of temperature was chosen to avoid the possibility of a reaction on alumina. The lower limit was the limit for a total conversion; at partial conversion, an accurate analysis of the three hydrocarbons could not be made. In the temperature range used, no variation of the reported ratios could be detected.

TABLE 5

Distribution of the Reaction Products in the Hydrogenolysis of 1,2-Dimethylcyclobutane on Platinum-Alumina Catalysts[a]

Catalysts	x_2/x_1	x_3/x_2	x_3/x_1
10% Pt	2.1 ± 0.1	1.45 ± 0.15	3.0 ± 0.3
0.2% Pt	1.95 ± 0.05	0.68 ± 0.06	1.3 ± 0.05

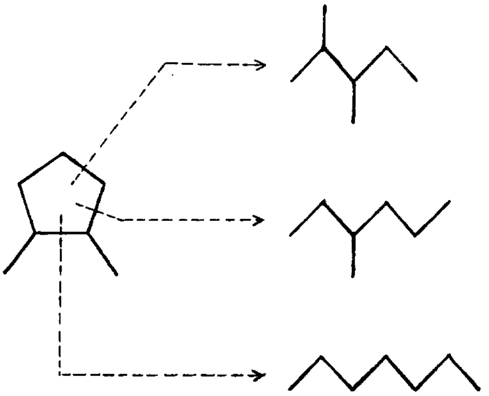
[a] x_1, x_2, x_3, are the concentrations of *n*-hexane, 3-methylpentane, and 2,3-dimethylbutane, respectively.

In this case again, the opening of a nonsubstituted cyclic bond, i.e., the formation of 2,3-dimethylbutane, was favored by a higher concentration of the platinum on the alumina.

Hydrogenolysis of 1,2-methylenemethylcyclobutane and of 1,2-dimethylcyclobutane gave the same product distribution. Thus, indifferently, either methylenemethylcyclobutane, or a mixture of *cis*- and *trans*-dimethylcyclobutanes, was used for the experiments. After partial hydrogenolysis of a mixture of cyclobutanes, the percentage of *cis* and *trans* in the unreacted dimethylcyclobutanes were, respectively, 20% and 80% (approximately equilibrium) instead of 60 and 40, as initially.

B. Hydrogenolysis of 1,2-Dimethylcyclopentane

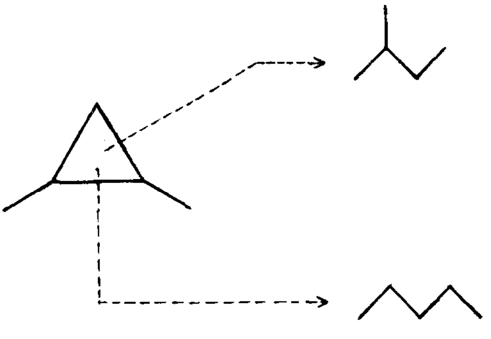
Three hydrocarbons, 3-methylhexane, *n*-heptane, and 2,3-dimethylpentane were formed in the hydrogenolysis of 1,2-dimethylcyclopentane, on a 0.2% platinum-alumina catalyst, at 320°C. Under these experimental conditions, the isomerization of the heptanes took place at an appreciable rate, so the initial distribution had to be considered; this latter was determined by extrapolating the distributions observed at different conversions. The initial distribution of hydrogenolysis was the same for the pure *cis* and for a mixture of *cis* and *trans* isomers. It roughly corresponded to an equal chance of rupturing the five cyclic bonds: 26% *n*-heptane, 43% 2,3-dimethylbutane, and 31% 3-methylpentane, instead of, respectively, 20%, 40%, 40% were obtained. The equilibration of the *cis*- and of the *trans*-dimethylcyclopentanes was complete under the same conditions.



C. Hydrogenolysis of cis- and trans-1,2-Dimethylcyclopropanes

The product distribution in the hydrogenolysis of *cis* and *trans* isomers was studied on metal films and platinum-alumina catalysts at total conversion.

In Table 6, the product distributions from *cis*- and *trans*-1,2-dimethylcyclopropanes are given on different metal films at various temperatures. On any metal, isopentane was



almost the only hydrocarbon obtained from *trans*-1,2-dimethylcyclopropane. On the contrary, *n*-pentane was also formed in the hydrogenolysis of the *cis* isomer and its amount increased with the temperature.

TABLE 6
Per Cent of *n*-Pentane in the Reaction Products of the Hydrogenolysis of 1,2-Dimethylcyclopropanes on Metal Films

Catalyst:	Platinum			Nickel			Palladium
T(°C):	50	20	0	48	23	0	25
cis:	23.4	19.2	15.9	12.7	8.9	2.6	9.1
trans:	2.9	0.4	0.9	0.6	0.5	—	0.5

Similar results were obtained on supported catalysts; on a 0.2% platinum-on-alumina catalyst, less than 1% of *n*-pentane was formed from the *trans*-dimethylcyclopropane, while in the hydrogenolysis of the *cis* isomer the amount of *n*-pentanes varied from 8% at 50°C to 19% at 120°C.

Some experiments at partial conversions on a 10% platinum-pumice catalyst showed that no *cis–trans* isomerization occurred on platinum; 14% of *n*-pentane at 73°C and 17% at 173°C were obtained from the *cis*-dimethylcyclopropane. In the hydrogenolysis of the *trans* isomer, the *n*-pentane could not be detected. It was verified that no isomerization of either cyclopropane took place on alumina up to 120°C and on pumice up to 180°C.

DISCUSSION

A comparison between the product distributions in the hydrogenolysis of methylcyclobutane (these results), and of methylcyclopentane on different platinum-alumina catalysts (*5*, *6*) shows that both hydrocarbons react in the same way, but at different temperatures.

On the other hand, the product distributions obtained from methylcyclobutane on a 1% platinum-alumina catalyst and on platinum films are very similar, and the same variation of distribution according to temperature is observed on both catalysts.

Thus, the reaction takes place on metal sites apparently and the same mechanisms are operating in the hydrogenolysis of methylcyclobutane and methylcyclopentane, on supported platinum catalysts and on platinum films.

Reaction Mechanisms

The results clearly show that the reaction of hydrogenolysis can be split up at least into three independent simultaneous reactions; the corresponding mechanisms and product distributions are referred to as Types A, B, and C.

Mechanism A is *nonselective:* it corresponds to an almost equal probability of breaking the cyclic bonds.

Mechanism B is *completely selective:* only disecondary bonds are broken, according to this mechanism.

Mechanism(s) C is *partly selective,* and involves the break of disecondary bonds mainly, but also of secondary–tertiary bonds.

Mechanism A is the major one on platinum and palladium films at the higher temperatures, and the only one on a 0.2% platinum on alumina; in this latter case, the observed distribution is independent of the conversion and of the temperature, in a large range of temperatures. This shows that Mechanism A is not composite and involves a single rate-determining step.

The selective mechanism B is operating on nickel at any temperature and on platinum films at the lower temperatures. The hydrogenolysis of methylcyclopentane on 10% platinum on alumina at 220°C gives also a typical B distribution: Isohexanes and not *n*-hexane are obtained as reaction products. Since on platinum film, Mechanism B is predominant at the lower temperatures and Mechanism A at the higher temperatures, the activation energy E_B associated with Mechanism B is smaller than E_A, activation energy associated with mechanism A.

It is necessary to introduce one or some other(s) mechanism(s), C, to explain the hydrogenolysis of methylcyclopentane on platinum catalysts. In the general case indeed, the observed distribution cannot be expressed as a linear combination of two independent distributions. Even when it is, as on 10% platinum on alumina below 300°C, the observed distribution is *not* the combination of distributions A and B, but of B and of another limit distribution. The activation energy associated with Mechanism(s), C, E_C, is intermediate between E_B and E_A.

Intermediate Species

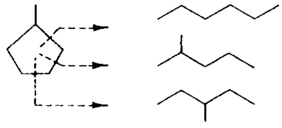
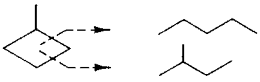
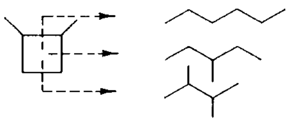
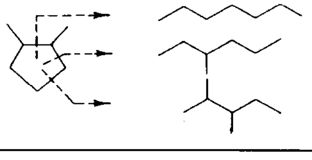
It is interesting to note that the ditertiary CH–CH bonds are also broken in the unselective type of hydrogenolysis (Type A). Table 7 shows the product distributions obtained on a 0.2% platinum-alumina catalyst from various substituted cyclopentanes and cyclobutanes.

Mechanism A affects every bond of the ring, even the ditertiary bonds, and the intermediate species corresponding to this mechanism should be a polyadsorbed species with only one C–H bond broken at each adsorbed carbon atom. α,β-Diadsorbed and α,β,γ-triadsorbed species, fulfilling this condition, could thus be responsible for the nonselective hydrogenolysis. However, the stereochemical properties of these species suggest that triadsorbed species and not diadsorbed species are correlated with Mechanism A.

α,β-Diadsorbed species were shown to be formed from cyclic hydrocarbons by the breaking of two *cis* C–H bonds (*14*). If diadsorbed species are responsible for the hydrogenolysis, there would be twice a chance of rupturing a disecondary CH_2–CH_2 bond than that of breaking a tertiary–secondary CH–CH_2 bond; ditertiary CHR–CHR bonds should only be broken if the two substituents R are in the *cis* position. At the same time *cis–trans* isomerization would be impossible with these species (*15*).

The hydrogenolysis of 1,2-dimethylcyclo-

TABLE 7
PRODUCT DISTRIBUTIONS CORRESPONDING TO MECHANISM A FOR DIFFERENT CYCLIC HYDROCARBONS

Reaction Product		Obtained %	Calculated %
	*n*-Hexane	38	40
	2-Methylpentane	41	40
	3-Methylpentane	21	20
	*n*-Pentane	53	50
	Isopentane	47	50
	*n*-Hexane	23.5	25
	3-Methylpentane	46	50
	2,3-Dimethylbutane	30.5	25
	*n*-Heptane	26	20
	3-Methylhexane	31	40
	2,3-Dimethylpentane	43	40

propane is an example in which α,β-diadsorbed species could be responsible for the reaction. The ditertiary cyclic bond of the molecule is broken only when the methyl groups are in *cis* position and no *cis–trans* isomerization is observed.

On the contrary α,β,γ-triadsorbed species are π-bonded to the surface (π-allylic species) (*16*); they are thought to be formed by losing hydrogen either from the top, or from the bottom of the molecule lying flat on the surface; reversely, they react either with adsorbed hydrogen atoms, or with molecular hydrogen. These two possibilities of attack (and of formation) determine the *cis–trans* isomerization of the disubstituted cycloalkanes (*15*, *16*). In hydrogenolysis, triadsorbed species would give an equal chance of rupturing any cyclic bond; the same product distribution should be obtained in the hydrogenolysis of *cis*- and *trans*-disubstituted cycloalkanes and *cis–trans* isomerization should accompany the reaction.

These are the characteristics of the hydrogenolysis of cyclopentanes, when Mechanism A is operating. Hydrogenolysis of *cis*- and *trans*-disubstituted cyclopentanes gives the same product distribution, with a complete equilibration of *cis* and *trans* isomers. On the other hand, the product distributions correspond to an equal chance of breaking any cyclic bond. Thus triadsorbed species, and not diadsorbed species, are responsible for the reaction. In the hydrogenolysis of cyclobutanes, similar results are obtained and similar conclusions can be reached: triadsorbed species are correlated with Type A hydrogenolysis.

Mechanism B of hydrogenolysis corresponds to a break of the disecondary CH_2–CH_2 cyclic bond exclusively. It is tempting to correlate this mechanism with an adsorbed species obtained from the molecules by losing four hydrogens on two carbon atoms. Such α,α,β,β-tetraadsorbed species were shown to be obtained from ethylene by dissociative adsorption on nickel and to be only slowly rehydrogenated (*17*). Anderson and Baker studied strong adsorption of propane and ethane (*18*) in the temperature range in which the hydrocracking of these hydrocarbons takes place; the adsorption corresponded to a lost of 3.5 to 5 hydrogen atoms on nickel and of 2 to 4 hydrogen atoms on platinum, per molecule of propane.

On rhodium, strongly adsorbed species are formed from *n*-hexane, including presumably α,α,β,β species (*19*); when heated, they further dissociated to irreversibly adsorbed species, which can only be hydrogenated to methane, after an extensive cracking. The present results show that irreversible species of the same nature are present on platinum, and this proves the existence on this catalyst of strongly adsorbed species such as α,α,β,β.

The following scheme summarizes the different mechanisms of hydrogenolysis and the different species involved:

$$\begin{tikzcd}
 & & & \text{Type A} & \\
\text{Gas} \arrow[r, shift left] & \alpha \arrow[l, shift left] \arrow[r, leftarrow, shift left] \arrow[d, shift right] & \alpha,\beta \arrow[l, leftarrow, shift left] \arrow[r, shift left] \arrow[d] & \alpha,\beta,\gamma \arrow[l, shift left] \arrow[u] & \\
 & \alpha,\alpha \arrow[u, shift right] \arrow[r] & \alpha,\alpha,\beta \arrow[r] & \alpha,\alpha,\beta,\beta \arrow[r] \arrow[d] & \text{Strongly adsorbed species} \arrow[d] \\
 & & & \text{Type B} & \text{Extensive cracking}
\end{tikzcd}$$

It includes α,β-diadsorbed and α,α,β-triadsorbed species, as precursors of Species A and B. These species in hydrogenolysis would lead to an unequal break of tertiary–secondary and disecondary bonds of the cycle, and thus could qualitatively explain the partly selective Type C hydrogenolysis; however, the distribution corresponding to this mechanism could not be directly determined and it is difficult to know which species is associated with Mechanism C.

The species intervening in hydrogenolysis are of two types: (1) on one hand, the same species as those responsible for the exchange reaction at a lower temperature, α,β-di-, α,β,γ-triadsorbed species; (2) on the other hand, the strongly adsorbed species, which do not play any part in the catalytic exchange, α,α,β-tri- and α,α,β,β-tetraadsorbed species. It could be possible that the intervention of the first type of species is limited to the hydrogenolysis of cyclic hydrocarbons; the strain of the ring, increased by the change of the hybridization state of two or three carbon atoms, is certainly an important factor determining the break of a C–C bond in a cyclic molecule. The other species α,α,β, and α,α,β,β certainly play a larger part in the hydrogenolysis of acyclic hydrocarbons.

The species of type (1) are in rapid interconversion and can be considered as in equilibrium with the gas phase (*20, 21*). On the contrary the rate of the interconversion between the strongly adsorbed species and the active mono- and diadsorbed species depends upon the temperature and the equilibrium is not reached between them (*19*).

Thus the hydrogen pressure dependency for Mechanism B should vary with the temperature; that could explain, in the hydrogenolysis of methylcyclobutane on platinum films, the change in the hydrogen pressure dependency of the selectivity factor with the temperature. However this change in the hydrogen pressure dependency can also be interpreted if three mechanisms are operating with different negative orders and if the part played by these different mechanisms alters as the temperature is increased.

Role of the Metal in Hydrogenolysis

A comparison between the product distributions on the different metal films gives further support to the supposed reaction mechanisms and intermediate species. The ability of the metals to determine a nonselective hydrogenolysis (Type A) is as follows:

$$\mathrm{Pd} > \mathrm{Pt} > \mathrm{Ni} \qquad \text{(I)}$$

The same is true for the metals supported on alumina (palladium and platinum). The reverse order corresponds to the selective mechanism of hydrogenolysis (Type B). On the other hand, the extensive cracking to methane also gives the latter classification, rhodium being added as the more cracking catalyst

$$\mathrm{Rh} > \mathrm{Ni} > \mathrm{Pt} > \mathrm{Pd} \qquad \text{(II)}$$

It is interesting to note that both classifications agree with our present knowledge of the species occurring on the different metals. Classification (I) corresponds to the relative ability of the different metals to form π-allylic adsorbed species (*15*), and the proposed mechanism for reaction A is thus substantiated.

The common precursor to both α,α,β and $\alpha,\alpha,\beta,\beta$ species and also to the irreversibly adsorbed species is the α,α-diadsorbed species discovered by Kemball in the exchange of methane. The Classification (2) given for the extensive cracking and the selective hydrogenolysis is the same as that given by Kemball for the multiple exchange of methane (*22*). It is therefore reasonable to suppose that α,α,β and $\alpha,\alpha,\beta,\beta$ species are responsible for the selective hydrogenolysis.

Role of the Carrier

In the discussion about the results on platinum-alumina catalysts, we have supposed, up to now, that alumina did not play any catalytic part in hydrogenolysis under our experimental conditions. The strong parallelism between platinum films and the 1% platinum-alumina catalyst, as far as the product distributions are concerned, was in our opinion a definite proof that hydrogenolysis exclusively takes place on the metal sites.

On the other hand, had alumina a catalytic activity, a dual function mechanism should be then involved: After dehydrogenation of the saturated hydrocarbon on platinum, the cyclic olefin would be cracked according to a carbonium ion mechanism on alumina and the acyclic olefins hydrogenated on platinum. Such a mechanism is ruled out by the results on alumina: In the temperature range of 120–250° in which methylcyclobutane is hydrogenolyzed on a platinum-alumina catalyst, methylcyclobutenes were not cracked on alumina; only a double-bond shift took place under these conditions. Similarly, double-bond shift and *no* cracking of methylcyclopentenes was observed on alumina at 220–400°, a temperature range in which the hydrogenolysis of methylcyclopentane occurs (*10*).

The parallelism between low content platinum-alumina catalysts and platinum films suggests that the catalytically activity sites on both catalysts are bonded to the same active centers. Spenadel and Boudart show that platinum in a 0.6% platinum-alumina catalyst was very dispersed on the carrier, in a quasi-atomic state (*7*). Thus the catalytic activity in metal films would also be localized to a few platinum atoms, supported on the inactive platinum carrier. This rather surprising result is good support for the theory of Rooney, which says that the different intermediate species, alkyl, π-olefinic, and π-allylic, shown to be formed on metal films, are bonded to the same single metal atom during their interconversion (*23*).

Similarly, the different behavior of the platinum-on-alumina catalysts with a high content of platinum could be explained by a larger size of the crystallites. On these catalysts, α,α,β and $\alpha,\alpha,\beta,\beta$ species are predominant; we believe that, whereas the bonding of the first type of species, α,β,γ species occurring in very dispersed catalyst, only involves one single metal atom, the species of the second type are bonded to two metal atoms. Since these metal atoms are not necessarily adjacent sites of the crystalline lattice, the importance of the size of the crystallites and consequently of the concentration of the metal on the carrier to determine such or such reaction, could be explained.

Of course, an induction by the alumina of the electronic properties of the supported metal could also be envisaged. But the main role of the alumina would be to disperse the platinum in smaller or larger crystallites, according to the concentration of the metal, thus favoring different types of species. If such an interpretation is correct, the selectivity in the hydrogenolysis of cyclic hydrocarbons could be used as a means of studying the state of the metal on the surface in various types of catalysts and particularly in supported catalysts.

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