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Reactions of Alkanes on Supported Pt-Au Alloys

J. R. H. VAN SCHAIK, R. P. DESSING AND V. PONEC[1]

Gorlaeus Laboratoria, P. O. Box 75, Leiden, the Netherlands

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Isomerization, dehydrocyclization and hydrogenolysis reactions of *n*-pentane and *n*-hexane were studied on supported Pt and Pt-Au alloys. The alloys studied were all in the composition range where this system is completely miscible (18% Pt in Au). Characteristic changes in selectivity towards the different reactions were observed when Pt was compared with alloys in the composition range 1-12.5% Pt and at temperatures 250-400°C: (a) extremely diluted Pt in Au (1-4%) mainly catalyses isomerization; (b) alloys with a composition around 10% Pt favor dehydrocyclization; (c) pure Pt shows mainly isomerization.

From the comparison of the *n*-pentane and *n*-hexane reactions it is possible to suggest a self-consistent picture of the mechanisms involved. For the alloys in (a) above the reaction mainly proceeds via a one-site isomerization mechanism. Catalysts in (b) are comparable to small particle catalysts and show cyclization and isomerization mainly via a cyclic mechanism. Pure Pt catalyses isomerization mainly via the bond shift mechanism ($\alpha\alpha$-γ adsorption) while ring closure probably proceeds via an $\alpha\alpha$-Ω adsorbed intermediate.

INTRODUCTION

Since the discovery (*1,2*) that platinum can catalyse reactions such as isomerization or ring enlargement, previously ascribed only to solid acids, skeletal rearrangement reactions of saturated hydrocarbons have been the subject of intensive research. It appears that these processes and also dehydrocyclization of alkanes are structure sensitive ("demanding") reactions. For example, it was found (*4*) that the isomerization of branched alkanes is faster on (111) crystallographic planes than on (100) oriented surfaces. The selectivity for isomerization, dehydrocyclization and cracking (hydrogenolysis) can be changed substantially when the crystal size of Pt particles on carriers is varied. Small particles strongly favor dehydrocyclization of hexane isomers to methylcyclopentane and benzene. From these results Anderson *et al.* (*3*) and Barron *et al.* (*5*) concluded that low-coordinated or even isolated Pt atoms are the best active sites for dehydrocyclization. It is, however, very difficult—if not impossible—to prepare a Pt catalyst with a high and controlled proportion of isolated Pt atoms. Owing to the practical and theoretical interest in Pt catalysts and skeletal rearrangement reactions, further research is necessary.

By alloying, a situation can be simulated which is akin to the extreme dilution of Pt on a carrier, particularly if one works with alloys where one component is inactive and where the active component is present in a low concentration. We have used to this end Pt-Au alloys in the concentration region 0-12.5 at.% Pt. In this region both components form a stable solid solution at temperatures around 400°C. In these alloys the dilution of Pt in the inert Au matrix is high and no complications caused by phase separation are expected. (The catalysts with 18-97 at.% Pt form two phases, viz, solutions of the indicated limit concentrations of Pt.)

The alloys were tested by reactions of two hydrocarbons: *n*-pentane and *n*-

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[1] To whom all correspondence should be directed.

hexane. Some experiments were also performed with methylcyclopentane. The reason for this choice was that *n*-pentane cannot isomerize via the cyclic intermediate proposed and proved by Barron and co-workers (*6*), while *n*-hexane has more reaction possibilities. The contribution of the mechanism via a cyclic intermediate to the total isomerization is a structure sensitive factor, so the comparison of the two hydrocarbons is interesting also from this point of view.

EXPERIMENTAL METHODS

Catalysts

Pt–Au alloys, supported on inert silica (250 mesh), were used as catalysts. They were prepared by chemical reduction according to the method of Kulifay (*7*). The ratio of metal to SiO_2 was about 16 wt%. First, a suspension is made from silica and a solution of hydrazine hydrochloride. Then, a solution of the platinum and gold chloride in the desired ratio is added with vigorous stirring to the suspension, kept at 80°C. After the reduction has been completed the system is neutralized with NH_4OH. The powder is then filtered, washed, dried and reduced by H_2 and equilibrated *in situ* at 430°C. The chemical and phase composition of the catalyst was checked by X-ray diffraction. (All compositions are given in at.%.) The variations in the lattice constants agreed reasonably well with the literature values and in no case was pure Pt or Pt-rich alloy detected.

Apparatus

About 1.5 g catalyst was used in a fixed bed reactor (cross section about 2 cm^2). The flow apparatus was the same as described previously (*8*). Partial pressure control of the hydrocarbon was achieved here by using two saturators in series, at different temperatures. The total gas flow was 6 ml/min in all experiments described below. The H_2/hydrocarbon ratio was kept constant at 17 for *n*-hexane, and 9 in experiments with *n*-pentane.

Materials

The hexane and pentane used (puriss) were from Fluka (Switzerland). The solutions of the gold and platinum chloride were prepared by dissolving Pt and Au in aqua regia.

Analysis

The product analysis was made using a Becker 409 gas chromatograph with a flame ionization detector. The column was a 9 m, 0.25 in., 20% squalane on Chromosorb W, 80 mesh. Column temperature was 60°C. The sensitivity of the detector for the different products was calibrated using pure components.

Data Evaluation

The experimental data were evaluated by using the following parameters (*8*). The overall conversion $\alpha(\%)$ of a hydrocarbon with *n* C-atoms is calculated as:

$$\alpha = 100 \sum_{i=1}^{n} \sum_{j,j\neq k}^{m} i\mathrm{C}_i^{(j)} \Big/ \left(\sum_{i=1}^{n} \sum_{j,j\neq k}^{m} iC^{(j)} + nC_n^{(k)} \right), \quad (1)$$

where i = number of C atoms in the molecules, C = molar concentration.

For a given i, the summation over j means that all m-hydrocarbons (e.g., for $i = 6$: benzene, cyclohexane, all methylpentanes, methylcyclopentane)[2] are included in the sum; k is the hydrocarbon in the feed. The index n is 5 for the reaction of pentane, 6 for reactions of hexane and methylcyclopentane. By evaluating α according

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[2] Unsaturated hydrocarbons are usually only present in small amounts at the highest temperatures used. They are counted in the sums as the respective saturated hydrocarbons.

to Eq. (1) one is actually making a material balance by counting the C-atoms present.

The parameter S_{tot}, the selectivity for all nondestructive reactions is defined as:

$$S_{tot} = n \cdot \sum_{j,j\neq k}^{m} C_n^{(j)} \Big/ \left(\sum_{j,j\neq k}^{m} \sum_{i=1}^{n} iC_i^{(j)} \right). \quad (2)$$

It is convenient to introduce the isomerization and cyclization selectivities, S_{is} and S_{cy}. The summation in the numerator of Eq. (2) for hexane is then made over methylpentanes for S_{is} and over methylcyclopentane, cyclohexane and benzene for S_{cy}. For pentane one uses the concentration of isopentane in S_{is} and of cyclopentane in S_{cy}. Further, it holds that $S_{tot} = S_{is} + S_{cy}$. The selectivity in cracking, S_{cr}, is defined by: $S_{tot} + S_{cr} = 1$.

To characterize the fission of the hydrocarbon chain the fission parameter M_f was introduced (*8,14*) where

$$M_f = \sum_{j}^{m} \sum_{i=2}^{n} (n-i)C_i^{(j)}/(C_1)_{\text{measured}}. \quad (3)$$

This parameter should be near to unity for terminal splitting, typical for nickel. When multiple fission is important, $M_f \ll 1$; when splitting is random or the bonds in the middle of the molecules have a higher chance to be broken, then $M_f \gg 1$.

All parameters mentioned are compared and evaluated for a constant feed and for very low conversions when consecutive reactions are of a small extent and the measured concentrations (conversion) are representative for the respective rates. In a flow system the reaction rate is calculated from the conversion α and the flow rate F (moles/sec). For conversions $< 10\%$ we may say that the rate per unit weight catalyst (w) is:

$$r_w = 10^{-2} d\alpha/d(w/F) \sim 10^{-2}\, \alpha \cdot F \cdot w^{-1}.$$

When α varied reversibly with the temperature (for $\alpha < 10\%$) the activation energy of the reaction was determined from the log α vs $1/T$ plot.

RESULTS

1. Reactions of *n*-Pentane on Pt Catalysts

Activity

With the amount of catalyst and the H_2 flow rate used, the conversion becomes measurable at temperatures of about 260°C. The conversion to the various gas products (see Table 1) is accompanied by self-poisoning. It was impossible to reach a steady state of the reaction and to determine, by measuring at various temperatures, a reliable value for the activation energy (E_a). A rough estimate of E_a gives a value between 30 and 40 kcal/mole. The deactivation of the catalyst is strongly accelerated above 330°C; most of the measurements were therefore limited to the temperatures between 260 and 330°C.

Selectivity

The initial product distributions (IPD) determined at $\alpha < 13\%$ are presented in Table 1. The total selectivity for all nondestructive reactions varies from 0.8 at 300°C to 0.7 at higher temperatures. Among the nondestructive rearrangements the isomerization is the most important ($S_{is} = 0.68$ at 298°C). The fission parameter $M_f \gg 1$. The ratio *n*-butane/propane, is about 0.2 and this indicates a clear selectivity in cracking: the bonds C_2–C_3 and C_3–C_4 have about a five-fold greater chance to be broken than the C_1–C_2, C_4–C_5 (terminal) bonds.

TABLE 1

PRODUCT DISTRIBUTION OF *n*-PENTANE ON Pt/SiO$_2$

T (°C)	Conv. (%)	C_1	C_2	C_3	nC_4	iC_5	cC_5[a]	S_{is}	S_{cy}
298	3.9	5	15	12	2	54	11	0.68	0.12
312	7.9	5	17	15	3	52	6	0.67	0.08
326	12.7	6	20	18	3	46	5	0.62	0.07
346	11.3	6	20	18	4	43	7	0.59	0.09

[a] cC_5 = cyclopentane.

TABLE 2
PRODUCT DISTRIBUTION OF *n*-PENTANE ON ALLOYS

Pt content (%)	T (°C)	Conv. (%)	C_1	C_2	C_3	nC_4	iC_5	cC_5[a]	S_{is}	S_{cy}
1	318	0.06					100		1.0	0
	343	0.11					100		1.0	0
	371	0.3					100		1.0	0
	398	0.6					100		1.0	0
2.5	350	0.35					100		1.0	0
	370	0.8			2	2	96		0.98	0
	400	2.6		1	2	2	95		0.97	0
	425	5.8	1	2	2	1	94	1	0.96	0.01
12.5	320	0.11	5	7	6	3	26	51	0.30	0.59
	348	0.9	4	8	7	5	22	53	0.26	0.61
	389	2.3	10	19	14	8	17	30	0.23	0.41
	417	7.0	21	27	17	13	3	18	0.05	0.29

[a] cC_5 = cyclopentane.

2. *n*-Pentane on Pt–Au Alloys

Activity

Three alloys were tested for this reaction: 1, 2.5 and 12.5 at.% Pt. With the amount of catalyst and flow rate used the conversion was readily measurable in the temperature range 340–400°C. In this temperature region and with the 1 and 2.5% Pt alloys a reproducible steady state conversion was reached from temperatures above and below, at each temperature. Some irreversible self-poisoning at higher temperature was observable on the 12.5% Pt alloy which also showed a remarkable increase in cracking above 360°C. The apparent activation energies found on these alloys are shown in Table 4.

Selectivity

The IPD are presented in Table 2. The most striking feature of these distributions is the complete absence of cracking reactions at steady state conversion on the most diluted Pt catalysts (1 and 2.5%). Also remarkable is the high selectivity for dehydrocyclization of the catalysts with 12.5% Pt. Comparing these catalysts with pure Pt we see that at $T < 360°C$ alloying leads to an increase in selectivity for nondestructive reactions (S_{tot}), this being mainly due to the increase in S_{cy}. The selectivity towards isomerization S_{is} is lower for the 12.5% Pt catalyst than for the Pt catalyst (Fig. 1).

When cracking is observed, the results are the same as for Pt catalysts, viz, $M_f \gg 1$; the bonds C_2–C_3 and C_3–C_4 break ($T < 350°C$) more easily than C_1–C_2 and C_4–C_5 bonds.

3. Reactions of *n*-Hexane on the Pt catalyst

Activity

Under the conditions used the reactions of *n*-hexane could be followed in the temperature region 260–310°C. However, as with *n*-pentane, the self-poisoning of the catalyst makes it impossible to determine an exact value for the activation energy. The activation energy of the total conversion of hexane was estimated to be between 30 and 40 kcal/mole. Self-

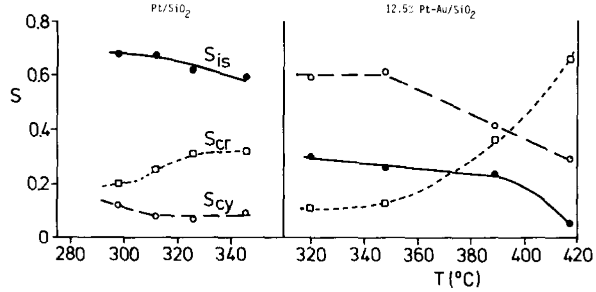

FIG. 1. Selectivity parameters (S_{is}, S_{cy}, S_{cr}) for *n*-pentane reactions as a function of temperature. Results for (pure Pt)/SiO_2 and (12.5% Pt–Au)/SiO_2 are presented.

TABLE 3
PRODUCT DISTRIBUTION OF n-HEXANE ON Pt/SiO_2[a]

T(°C)	Conv. (%)	C_1	C_2	C_3	C_4	C_5	2mP	3mP	MCP	Be	S_{is}	S_{cy}
274	0.5	14	7	16	6	10	23	16	7	0	0.57	0.10
294	3.7	4	6	17	7	7	30	18	7	2	0.58	0.12
311	11.6	5	7	18	9	5	30	19	6	2	0.60	0.09

[a] mP = methylpentane; MCP = methylcyclopentane; Be = benzene.

poisoning became quite severe at temperatures above 310°C.

Selectivity

The IPD observed on Pt at various temperatures are presented in Table 3. The selectivity parameters (S_{cy}, S_{cr} and S_{is}) are almost independent of temperature. As with pentane, isomerization is the most important reaction on the pure Pt catalyst. In all cases the fission parameter $M_f \gg 1$. The relative reactivity towards breaking various bonds upon hydrogenolysis of the n-hexane molecule can be estimated from the ratio of the particular cracking products. It can be seen that the chance to split the C_3–C_4 bond is about twice as large as the chance to break the remaining bonds. The ratio C_4–C_5 increases with the increasing temperature. Consecutive reactions of pentane possibly play a role, because in the same temperature region pentane is reactive as well.

4. Reactions of n-Hexane on Pt–Au Alloys

Activity

The following alloys were tested by the reactions of hexane: 1.0, 2.5, 3.7, 8.0 and 12.5 at.% Pt in the alloy. Under the conditions used, the activity of these alloys could be studied in the temperature range 300–400°C. At low conversions the variation in the activity with temperature was completely reversible, in contrast to the Pt catalyst. Self-poisoning plays practically no role here. This fact allows us to determine the apparent activation energy E_a of the total conversion. The values of E_a are collected in Table 4, together with the values for the n-pentane conversion.

Selectivity

The initial product distributions as obtained at various temperatures on a number of alloys are summarized in Table 5. It is shown that the total selectivity for all nondestructive reactions is higher on alloys than on Pt catalysts ($S_{tot} > 0.9$). In comparison with pure Pt the various alloys show a better selectivity for isomerization (2.5% Pt–Au) and dehydrocyclization (12.5% Pt–Au).

Figure 2 shows the comparison of selectivities for Pt and two alloys as a function of temperature.

5. Reactions of Methylcyclopentane

Because intermediates with a structure resembling that of methylcyclopentane can play an important role in isomerization of n-hexane, we determined the IPD for the reaction of MCP with H_2 on the highly

TABLE 4
APPARENT ACTIVATION ENERGIES FOR n-PENTANE AND n-HEXANE REACTIONS

	E_a	
Alloy % Pt	n-Hexane	n-Pentane
1	26	24
2.5	25	27
8.5	31	
12.5	37	35

TABLE 5
PRODUCT DISTRIBUTION OF *n*-HEXANE ON ALLOYS

Alloy % Pt	T (°C)	Conv. (%)	C_1	C_2	C_3	C_4	C_5	2mP	3mP	MCP	Be	S_{is}	S_{cy}
1	388	0.8	0	4	4	2	2	30	43	10	3	0.76	0.14
	403	1.3	1	1	2	1	1	35	43	11	4	0.79	0.16
2.5	305	0.1	—	—	—	—	—	60	40	—	—	1.0	0.0
	353	0.5	—	8	4	—	—	50	37	—	—	0.97	0.0
	395	2.0	3	1	8	1	1	46	39	—	—	0.95	0.0
3.7	318	0.1	36	6	—	—	—	48	11	—	—	0.88	0.0
	349	0.2	34	—	—	—	—	45	21	—	—	0.92	0.0
8	320	0.2	31	4	3	—	9	21	30	—	—	0.90	0.0
	358	1.1	6	1	2	—	—	33	38	15	4	0.76	0.21
	400	3.8	1	1	2	—	1	37	38	16	3	0.78	0.20
12.5	370	0.6	2	4	6	4	2	10	34	32	4	0.50	0.40
	390	1.5	3	2	5	2	3	8	29	40	5	0.41	0.49

diluted Pt alloy (2.5%) which showed such a high selectivity for isomerization. For example, at 359°C and a total steady state conversion α of 2.7% there was no detectable cracking. Except for traces of 2-methylpentane (ring opening) the reaction products contain only products of one reaction, namely, ring enlargement (77% to benzene and 22% to cyclohexane). The ratio benzene/cyclohexane is a function of temperature, increasing at higher temperatures.

6. "Background" Reactions

In this work catalysts on inert SiO_2 as a carrier were used. This silica was found to be completely inactive up to a temperature of 450°C. However, because there was a danger that during the catalyst preparation the acidity of the silica surface might increase, a check for a possible dual function behavior of the catalyst was performed. *n*-Pentane and *n*-pentene-1 were led over a Au/SiO_2 catalyst prepared in the same way as described before. Below 430°C no isomerization to branched pentanes (pentenes) or cyclization could be detected.

DISCUSSION

The most relevant results of this paper are summarized in Fig. 3. The selectivity parameters S_{is}, S_{cy} and S_{cr} are plotted as a function of the alloy composition for *n*-hexane. The lines drawn indicate the di-

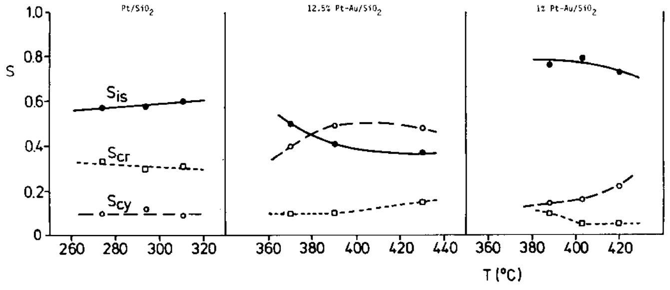

FIG. 2. Selectivity parameters (S_{is}, S_{cy}, S_{cr}) for *n*-hexane reactions as a function of temperature. Results for (pure Pt)/SiO_2, (12.5% Pt–Au)/SiO_2 and (1% Pt–Au)/SiO_2 are presented.

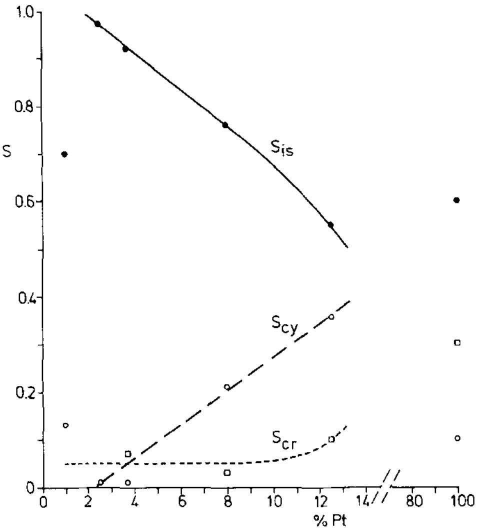

FIG. 3. Selectivity parameters (S_{is}, S_{cy}, S_{cr}) for *n*-hexane reactions as a function of alloy composition (the values are compared at $T \sim 360°C$).

rection of the changes in the selectivity parameters upon changes in the alloy composition.

In principle, the variations in the selectivity may be caused by two effects, namely *geometric* and *electronic* effects. By bringing the active component (Pt) into an inactive matrix (Au) the number of available active sites is reduced and the spatial distribution of active sites is altered (the mean size of ensembles of active sites is reduced, the mutual distance of ensembles increased). High dilution of the active compounds inhibits preferentially those reactions or reaction pathways which require ensembles with a higher number of active sites for the formation of the transition complexes. Alloying also changes the electronic structure of metals; sometimes even a redistribution of electrons among various orbitals takes place. Shifts in the position of electron energy levels are reflected by the altered chemisorption bond strength, which in its turn influences the reactivity of adsorbed species and may determine the activation energy, the reaction pathway of further reactions, etc. It is impossible to separate completely the geometric and electronic effects; nevertheless, we shall make an attempt below to estimate their relative importance for the reactions on the diluted Pt–Au alloys.

The mutual influence and the strength of interaction in Pt–Au alloys is classified in the literature as rather weak (*9,10*). The formation of Pt–Au alloys is endothermic ($\Delta H > 0$). At low temperatures (around 400°C) two phases are simultaneously present with 18 and 97 at.% Pt. By analogy with the Ni–Cu system, the formation of Pt clusters is plausible and isolated Pt atoms are to be expected only at the highest dilutions. Magnetic measurements (*10*) showed the largest variation in the magnetic susceptibility to occur at the lowest Au concentrations, while in the region of the highest dilution of Pt in Au the susceptibility varies only marginally. Therefore, with respect to the electronic structure a much larger difference should be expected between Pt and the 12.5% Pt alloy than between the 12.5 and 2.5% Pt alloy.

However, the product distributions presented in this paper show the most pronounced variations in selectivity to occur just in the region of very diluted alloys, while the 12.5% Pt alloy resembles the pure catalyst. Therefore, we believe it is justified to attempt the explanation of the variation in selectivity mainly in terms of the number and spatial distribution of active (Pt) sites.

Once this idea is accepted, the next step is straightforward: it would appear that isomerization (and possibly ring enlargement) makes use of the smallest ensembles of active sites (maybe even of isolated Pt atoms). Dehydrocylization would demand ensembles of a larger size, while the ensembles required for cracking (hydrogenolysis) would be still larger.

Let us investigate now if we can find a support for these ideas in the literature on this problem, or possibly to derive conclusions on the basis of the results presented with regard to the various mechanisms suggested in the literature.

There are basically three mechanisms suggested for isomerization, which is the reaction prevailing in the most diluted alloys.

1. The Anderson–Avery (*11*) *bond shift* mechanism. The main feature of this mechanism is that at least *three* C–H bonds must dissociate first and the arising hydrocarbon radical occupies at least *two* sites. A certain portion of these intermediates reacts always up to the cracking products.

2. Reaction via the *cyclic intermediate* [according to Barron *et al.* (*6*)]. In their paper the authors (*6*) do not specify the mode of adsorption of these cyclic intermediates but according to later papers by Barron *et al.* (*5*) the following can be added. The small crystallites of Pt prefer isomerization via a cyclic intermediate (*12*) and according to Anderson *et al.* (*3*) the formation of final gaseous cyclic products is also favored when smaller crystallites of Pt are used as catalysts. The cyclic intermediate can be formed by an αα-Ω ring closure using *one* or *two* active Pt sites for hydrocarbon adsorption, which according to Anderson *et al.* (*3*) can be indicated schematically (Fig. 4). Again, at least *three* C–H bonds have to be broken and hydrogen must be adsorbed somewhere before the ring closure takes place.

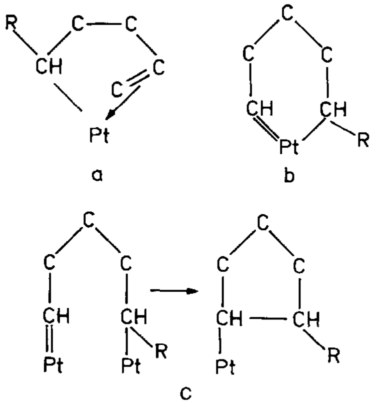

FIG. 4. Schematic representation of a αα-Ω ring closure: (a,b) using one Pt atom; (c) using two Pt atoms.

3. *Carbonium ion-like* mechanism [according to McKervey *et al.* (*13*)]. This mechanism has been suggested in order to explain why certain bridged hydrocarbons can isomerize easily while they exchange with deuterium only one H atom at each residence on the surface. This "*one site*" mechanism with a low degree of dissociation (*one* C–H bond) stems from the same basic idea of an alkyl shift as the bond shift mechanism. Schematically, this is shown in Fig. 5.

The last mentioned mechanism is thus able to operate, hypothetically, also on the most diluted alloys. If we assume that it is really so, we can develop (as shown below) a self-consistent picture of the behavior of alloys studied in this paper.

Let us discuss now the results obtained on the other extreme of our alloy series; namely, the pure Pt catalyst. Compared to the most diluted alloys the activation energy increases (see Table 4) and among the products the cyclic ones appear. Moreover, we observe that S_{is} and S_{cy} are both independent of temperature which indicates a common intermediate for both reactions, isomerization and dehydrocyclization. However, this must be an intermediate different from the one which operates on the most diluted alloys where only isomerization occurs. We have two possibilities for this process, described above in points (1) and (2). Let us see whether we can discriminate between these two possibilities.

One of the hydrocarbons studied here, *n*-pentane, can isomerize only according to mechanisms 1 (bond shift) or 3 (carbonium

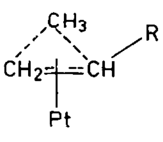

FIGURE 5.

ion-like), but not via mechanism 2. Because mechanism 3 is the better candidate for explanation of data on the most diluted alloys where no dehydrocyclization occurs, we believe that the best choice is to suggest mechanism 1 as prevailing on "massive" Pt catalysts and mechanism 3 as prevailing on the most diluted alloys (isolated Pt atoms). As can be seen on Pt catalysts the behavior (S_{is}, S_{cy}) of *n*-pentane and *n*-hexane is very similar (Figs. 1 and 2). We are, therefore, inclined to believe that also *n*-hexane reacts here via the same reaction path as pentane, i.e., mechanism 1. The suggestions made in the literature offer indeed a form for a "common" intermediate for isomerization and dehydrocyclization by the Pt catalyst. If we compare the $\alpha\alpha,\gamma$-intermediate for the bond shift isomerization and the $\alpha\alpha,\Omega$-intermediates of ring closure according to Barron *et al.* (*5*) (see Fig. 4), we see that there is a great resemblance between these two intermediates, as in the number of necessary sites and the way of further reaction.

The catalyst with the composition around 10% Pt reveals the following interesting feature. In contrast to Pt or very diluted alloys, we observe here a characteristic *difference* between *n*-hexane and *n*-pentane in the selectivity. For example, at 350°C on a 12.5% Pt alloy:

	S_{cy}	S_{is}
n-pentane	0.6	0.3
n-hexane	0.3	0.6

At first sight, *n*-pentane seems to be better suited for dehydrocyclization by these particular catalysts than *n*-hexane. However, this could be only apparent. It is known that on small metal particles a mechanism of isomerization via the cyclic intermediate is favored. Following this idea we can understand the results of the last table also by assuming that actually a part of the cyclic intermediates (methylcyclopentane-like) leads to the isomerization products, so that the "extra" activity of the 12.5% Pt alloy in cyclization of *n*-pentane manifests itself in the reactions of *n*-hexane by isomerization and not cyclization products.

In summarizing the discussion, we come to the following conclusions. We distinguish three different groups of the catalysts studied here:

1. Pure platinum. The prevailing reaction is isomerization and cyclization. The prevailing mechanisms are bond shift for isomerization ($\alpha\alpha,\gamma$) and ring closure by an $\alpha\alpha,\Omega$ adsorption (Fig. 4).
2. Catalysts with about 10% Pt. The prevailing reaction is cyclization and also the isomerization proceeds partially via a cyclic intermediate. These catalysts remind one strongly of Pt catalysts with small particles [ultrathin films (*3*), 0.2% Pt–Al_2O_3 (*5*)].
3. Most diluted alloys (1–4% Pt). The highly prevailing (or sometimes exclusive) reactions are isomerization and ring enlargement. In view of the extreme dilution the most probable mechanism is the one-site carbonium ion-like mechanism (Fig. 5).

The authors are aware of the fact that some of the conclusions made need further support by more experiments and also the characterization of the catalysts calls for further study. This work is in progress in our laboratory.

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