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# Relation Between Catalytic Properties and Structure of Metal Films

## II. Skeletal Reactions of Some $C_6$ Alkanes

J. R. ANDERSON,* R. J. MACDONALD, AND Y. SHIMOYAMA

*School of Physical Sciences, Flinders University, Adelaide, South Australia*

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Skeletal isomerization, cyclization, and hydrogenolysis reactions of *n*-hexane and 2-methylpentane have been studied on various platinum and nickel film catalysts which were prepared under UHV conditions. The reactions were carried out in the presence of excess hydrogen in a static system at 273°C, and conversions were restricted to $<5\%$. The work particularly compared the catalytic behavior of ultra-thin and thick films, where in the former the *average* metal density on the substrate was of the order of a monolayer. Nevertheless, these ultra-thin films actually consist of crystals $<20$ Å across, possibly together with monodispersed platinum atoms.

The most detailed information was obtained from the reactions of *n*-hexane. On all nickel films hydrogenolysis (mainly to methane) was the dominant reaction, while on all platinum films the formation of $C_6$ isomerization and cyclization products was the more important. Nevertheless, with both metals the reaction over ultra-thin films had a much higher selectivity for the formation of $C_6$ products versus hydrogenolysis products than did the reaction over various thick films. Furthermore, ultra-thin platinum films gave an increased proportion of cyclic $C_6$ products compared to thick films. The variation in catalytic selectivity, particularly with platinum, is interpreted on the following model: (i) the very small crystals of the ultra-thin films present an increased proportion of low-coordinated corner atoms, (ii) these corner atoms favor the formation of adsorbed carbocyclic reaction intermediates: these intermediates can lead to cyclic reaction products as well as providing a contributing path for isomerization, (iii) hydrogenolysis as well as isomerization by a C–C bond shift mechanism are not favored by corner atoms, but require two or three adjacent platinum atoms on a crystal face; the triadsorbed intermediate which requires three platinum atoms is favored by a (111) face or facet, and itself favors isomerization by C–C bond shift versus hydrogenolysis. Because the selectivities (versus hydrogenolysis) for isomerization by an adsorbed carbocyclic intermediate and by C–C bond shift vary in different ways with the concentration of low coordinated corner platinum atoms, and because the relative importance of these two isomerization paths are influenced by hydrocarbon geometry, the overall dependence of selectivity on catalyst structure may, for a given hydrocarbon, be complex, and requires analysis in terms of the contributing mechanisms.

Reactions with 2-methylpentane were so heavily in favor of the formation of methylcyclopentane that the dependence on films structure was not large.

UHV ultra-thin films form a useful model system for studying the effects of particle size on catalyst selectivity without the complication due to possible surface contamination.

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* Present address: CSIRO Division of Tribophysics, University of Melbourne.

## INTRODUCTION

The work in Part I (*1*) of this series was approached with the object of differentiating between the catalytic behavior of (hopefully) near ideal low index surfaces such as (111) and (100) planes of nickel on the one hand, and surfaces of lesser perfection such as may be present in random polycrystalline films, on the other hand; included in this latter category are higher index surface planes, as well as generally occurring crystallographic surface imperfections. A distinction which runs parallel to this classification is the extent of occurrence in the surface of metal atoms with a coordination number that is low compared to the value for an atom in a low index plane. However, when using thick random polycrystalline films as a source of imperfect catalyst surfaces, any degree of precise experimental control over the nature and extent of the surface imperfection is extremely difficult.

To investigate the catalytic influence of low coordination atoms, we have elected at this juncture to proceed by the use of a film structure where the concentration of atoms of low coordination is necessarily relatively high, yet where the method of film preparation offers hope that a reasonable degree of control over film structure might eventually be achieved; that is, by the use of ultra-thin metal film catalysts where the *average* surface concentration of metal atoms on the substrate is of the order of one monolayer. The preparation and use of ultra-thin films as models for supported catalysts has recently been described by Anderson and MacDonald (*3*). We have made a comparison between the behavior of these films and conventional thick (111), (100), and polycrystalline films of the type described previously (*1*) (*2*). Nevertheless, for the present purpose we have also recognized that thick evaporated metal films, as normally prepared, inevitably have an edge region where the thickness changes from thick to ultra-thin and so, unless special precautions are taken, some ultra-thin film in the edge region may well contribute to the overall behavior of the catalyst. The present paper, therefore, also describes attempts we have made to prepare thick films which do not have an appreciable contribution from an ultra-thin component.

The reactions considered in the present paper use *n*-hexane and 2-methylpentane as reactants (in each case in the presence of excess hydrogen) with films of platinum and nickel. We are concerned with reactions involving the carbon skeletons of these molecules, mainly skeletal isomerization, hydrogenolysis, and dehydrocyclization. Although one of our main purposes is to evaluate the dependence of these reactions on catalyst structure, we must emphasize from the outset that, even though one may be dealing with two apparently quite similar reactants, the influence of catalyst structure must still be considered in detail only with respect to a specific reactant. For instance, with the present reactions it emerges that the behavior of *n*-hexane is much more strongly dependent on catalyst structure than is 2-methylpentane, largely because the reaction of the latter is overwhelmingly dominated by a single reaction pathway.

## EXPERIMENTAL METHODS

The films were prepared under UHV conditions and the general layout of the system was the same as in Part I. Ultra-thin films were prepared and used in the reaction vessel described previously by Anderson and Macdonald (*3*), and the metal evaporation techniques for the various types of films have been previously described (*1–3*). The 2-methylpentane sample was of high purity, bought from the National Physical Laboratory, England, and the *n*-hexane was Research Grade from Phillips Petroleum Co.

We distinguish the following types of film catalysts upon which the reaction has been studied: (i) ultra-thin films deposited on mica at 275°C; (ii) "normal" thick polycrystalline films deposited on glass at 0°C; (iii) "normal" thick films exposing mainly (111) surface and formed by deposition on mica at 300°C; (iv) "normal" thick films exposing mainly (100) surface and formed by deposition on a layer of evaporated sodium chloride at 250°C; and (v) "fringe-free" thick polycrystalline films, also prepared by a technique described below and deposited on glass at 275°C; the term "fringe-free" is used to indicate that the film was designed to have no appreciable contribution from a very thin edge region. Although we have designated films of the latter type as polycrystalline, the deposition temperature of 275°C results in a substantial degree of preferred orientation to expose an enhanced proportion of (111) surface compared to a polycrystalline film deposited at 0°C. In film types (ii)–(iv) the term "normal" is used to indicate the use of a reaction vessel of conventional cylindrical design (*1*, *2*) where some contributions from very thin edge regions are to be expected. The techniques for preparing and identifying the (111), (100), and polycrystalline films were the same as previously described (*1*, *2*) and the methods will not be repeated here. X-Ray fluorescence analysis of the composition of the platinum films showed tungsten (from the evaporation source) to be present to no more than 0.25%.

Ideally, the preparation of "fringe-free" films would require evaporation from a point source onto the inside wall of a spherical vessel without the presence in the wall of ports to attached tubulation etc., which result in film edge regions. The latter condition is, of course, an impossibility. Moreover, evaporation is inconvenient (particularly with platinum) from anything approaching a point source. The compromise solution we have adopted is shown in Fig. 1. The cylindrical feature of the reaction vessel is designed to be compatible with the geometry of the filament evaporator, while the spherical sections at top and bottom were designed to eliminate corner regions and to obtain an approximately uniform film thickness over the entire film. Except for an extremely small and abrupt edge region at the lip (A), the only region where the metal varies from thick to very thin is at the edge of that metal which is deposited on the glass baffle area (B), and this is also very small. In use, all of the metal on B could be eliminated as a region of active catalyst by cooling B to about room temperature by circulating cooling water through the reentrant volume V; however, we deemed this not to be necessary in the present work. The total geometric area of film was estimated at 120 cm$^2$. Because of the sections of spherical surface in this vessel, mica substrates could not be usefully used, and we have limited the use of the vessel to the preparation of thick polycrystalline films (20–25 mg), deposited with the glass substrate at 275°C under UHV conditions. In the work to be described in this paper, "fringe-free" films were limited to platinum.

With all film catalysts, the composition of the reaction mixture was monitored via a Metrosil pellet leak to an MS10 mass spectrometer, while a break-seal could be used to extract reaction mixture for VPC analysis. For this purpose a Perkin-Elmer Model F11 chromatograph was used, together with a 200 ft × 0.01-in. capillary column coated with Perkin-Elmer "HHK" operated at a column temperature of 10 to 25°C.

It is important to recognize that our reaction mixtures were prepared under completely mercury-free conditions, and by the

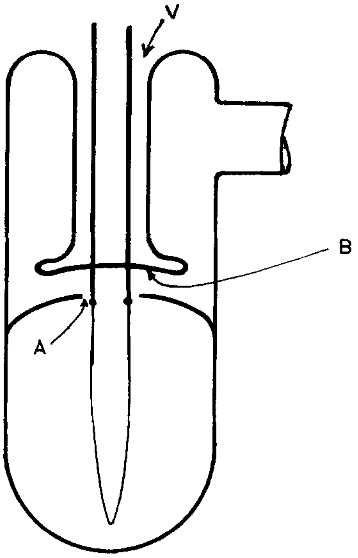

FIG. 1. Reaction cell for use with "fringe-free" films.

TABLE 1

Reaction of *n*-Hexane Over Platinum Film Catalysts: $C_6$ Reaction Products[a]

| Type of catalyst and expt no. | Reaction temp (°C) | $C_6$ reaction products (mole %) 2-MP | 3-MP | 2,3-DMB, neo-H, CHe | MCP | CH + B | Total conversion (%) | Selectivity |
|---|---|---|---|---|---|---|---|---|
| Pt 1, ultra-thin film, 0.32 μg $cm^{-2}$, deposited 275°C | 273 | 10.5 | 4.5 | 0 | 73.7 | 11.3 | 0.77 | >10 |
| Pt 2, 0.84 275°C | 273 | 12.5 | 5.6 | 0 | 72.4 | 9.5 | 3.3 | >10 |
| Pt 3, 0.25 20°C | 273 | 13.9 | 5.4 | 0 | 72.9 | 8.0 | 1.0 | 17.1 |
| Pt 4, 1.0 20°C | 273 | 17.6 | 6.4 | 0 | 69.6 | 6.4 | 1.0 | 11.6 |
| Pt 5, polycrystalline film, ~0.1 mg $cm^{-2}$, deposited 0°C | 273 | 25.5 | 11.7 | 0 | 47.6 | 15.2 | 1.75 | <2 |
| Pt 6, 0°C | 273 | 23.9 | 10.6 | 0 | 52.0 | 13.5 | 0.74 | <2 |
| Pt 7, 0°C | 273 | 32.4 | 14.7 | 0 | 41.0 | 11.9 | 4.9 | <2 |
| Pt 8, 275°C | 273 | 39.0 | 19.0 | 0 | 27.0 | 14.0 | 1.2 | 1.8 |
| Pt 9, 275°C | 273 | 34.0 | 17.0 | 0 | 34.0 | 15.0 | 1.3 | 1.0 |
| Pt 10, (111) film, ~0.1 mg $cm^{-2}$, deposited 300°C | 273 | 33.4 | 14.4 | 0 | 38.9 | 13.3 | 3.0 | <5 |
| Pt 11, 300°C | 273 | 27.8 | 14.7 | 0 | 41.0 | 16.5 | 3.8 | <5 |
| Pt 12, (100) film, ~0.1 mg $cm^{-2}$, deposited 250°C | 273 | 22.5 | 11.6 | 0 | 53.3 | 12.6 | 2.7 | <5 |
| Pt 13, 250°C | 273 | 21.5 | 11.6 | 0 | 43.7 | 23.2 | 1.6 | <5 |
| Pt 14 (nine expts.), "fringe-free" films, ~0.3 mg $cm^{-2}$, –Pt 22 deposited at 275°C | 273 | 43<br>–20 | 22<br>–11 | 0 | 10<br>–50 | 16<br>–19 | 0.5<br>–2.0 | Not available |

[a] 2-MP = 2-methylpentane; 3-MP = 3-methylpentane; 2,3-DMB = 2,3-dimethylbutane; neo-H = neohexane; MCP = methylcyclopentane; CH = cyclohexane; B = benzene; CHe = cyclohexene.

use of metal valves and good vacuum technique in the gas handling line we estimate that adventitious impurity in the reaction mixture would not have exceeded about 1 part in $10^7$–$10^8$. The only significant impurities in the reaction mixtures came from small amounts of hydrocarbons in the parent hydrocarbon samples: *n*-hexane, 0.036% 3-methylpentane; 2-methylpentane, 0.016% cyclopentane and 0.009% *n*-pentane. Kinetically these impurities were of negligible importance, and corrections for them were made when evaluating the analytical data.

Product analyses were obtained by a combination of VP chromatography and mass spectrometry. VPC retention times were calibrated using pure known materials, while sensitivity factors for components were obtained from the data of Dietz (*4*) for the flame-ionization detector. Quantitative data from the VP chromatograms were obtained from peak areas either by electronic integration or by cutting the chart and weighing. Mass spectral data were obtained at 50 eV on the ionizing electrons, with fragmentation corrections and sensitivity calibrations obtained from both known compounds and from API data (*5*). In general, most reliance was placed on VPC data for $C_5$ and $C_6$ products, although mass spectrometry was useful in providing extra data for benzene and cyclohexane: mass spectrometry was relied on entirely for methane, while data from both methods was used with ethane, propane, and the butanes.

## RESULTS

### 1. *Reactions Over Platinum Film Catalysts*

For all reactions, the initial reaction mixtures contained a hydrogen/hydrocarbon molar ratio of 10:1, and at the reaction temperature the total initial pressure in the reaction vessel was approximately 60 Torr. The effective reaction volumes were approximately the same for all systems, and the reaction volume is estimated to contain initially about $3.6 \times 10^{20}$ $H_2$ molecules and $3.6 \times 10^{19}$ *n*-hexane molecules. Reactions were carried out for about 30 min, and the extent of reaction generally was limited to $<5\%$.

The results of reactions over various platinum films are contained in Tables 1, 2, and 3, for various types of platinum films including both ultra-thin films and thick films. Table 1 records the proportions of the various $C_6$ reaction products from *n*-hexane, while Table 2 shows the proportions of the various $C_1$–$C_5$ hydrogenolysis products. Table 3 contains similar data for reactions with 2-methylpentane. Table 1 also records the reaction selectivity, defined as the ratio of the number of *n*-hexane molecules reacting to $C_6$ products to the number of *n*-hexane molecules reacting to give $C_1$–$C_5$ products.

The reproducibility of the reaction over the ultra-thin films and over most of the thick films was satisfactory: however, the "fringe-free" films showed a spread in the distribution of reaction products, so in Table 1 we only record the observed range for each product. The reproducibility of "fringe-free" films for the reaction of 2-methylpentane (Table 3) was considerably better, but is no doubt a consequence of the simplicity of the reaction product distribution in which only one product (methylcyclopentane) is of overwhelming importance.

### 2. *Reactions Over Nickel Film Catalysts*

The results of reactions over various nickel film catalysts are given in Tables 4 and 5, where again we include the behavior of ultra-thin films and various types of thick films. The selectivity in Table 4 is defined in the same way as for Table 1.

## DISCUSSION

From the known way in which the early growth of evaporated metal films occurs (*6*), one would expect the ultra-thin films to consist of extremely small isolated crystallites, possibly accompanied by isolated metal atoms, distributed over the substrate. In fact, we were able to resolve the structure of some ultra-thin films recorded in Tables 1–5 by electron microscopy (as well as some other films of similar

TABLE 2

REACTION OF *n*-HEXANE OVER PLATINUM FILM CATALYSTS: $C_1$–$C_5$ REACTION PRODUCTS[a]

| Type of catalyst and expt. no. | Reaction temp (°C) | $C_1$–$C_5$ reaction products (mole %) M | E | P | n-B | iso-B, neo-P | n-P | iso-P | CP |
|---|---|---|---|---|---|---|---|---|---|
| Pt 1, ultra-thin film, 0.32 μg $cm^{-2}$, deposited 275°C | 273 | ~26 | 26 | 33 | 9.1 | 0 | 5.6 | 0 | 0.3 |
| Pt 2, 0.84 275°C | 273 | ~32 | 8.0 | 37 | 12.4 | 0 | 9.0 | 0 | 1.7 |
| Pt 3, 0.25 20°C | 273 | 12 | 12.5 | 42 | 21 | 0 | 12.5 | 0 | 0 |
| Pt 4, 1.0 20°C | 273 | 43 | 10.5 | 27.4 | 11.4 | 0 | 7.7 | 0 | 0 |
| Pt 5, Pt 6, Pt 7, polycrystalline films, ~0.1 mg $cm^{-2}$, deposited 0°C | 273 | ~52 | 26 | 8 | 5 | 0 | 8 | 0.2 | 0.5 |
| Pt 8, and Pt 9, 275°C | 273 | 36 | 12 | 19 | 15 | 0 | 18 | 0 | 0.4 |
| Pt 10 and Pt 11, (111) films, ~0.1 mg $cm^{-2}$, deposited 300°C | 273 | ~40 | 19 | 21 | 6 | 0 | 13 | 0.3 | 1 |
| Pt 12 and Pt 13, (100) films, ~0.1 mg $cm^{-2}$, deposited 250°C | 273 | ~38 | 18 | 23 | 9 | 0 | 10 | 0.5 | 1.3 |

[a] M = methane; E = ethane; P = propane; n-B = *n*-butane; iso-B = isobutane; n-P = *n*-pentane; iso-P = isopentane; CP = cyclopentane; neo-P = neopentane.

TABLE 3

REACTION OF 2-METHYLPENTANE OVER PLATINUM FILM CATALYSTS: $C_6$ REACTION PRODUCTS[a]

| Type of catalyst and expt. no. | Reaction temp (°C) | $C_6$ reaction products (mole %) | | | | | Conversion to $C_6$ products (%) |
|---|---|---|---|---|---|---|---|
| | | n-H | 3-MP | 2,3-DMB, neo-H, CHe | MCP | CH plus B | |
| Pt 20, polycrystalline film, ~0.1 mg $cm^{-2}$, deposited 0°C | 273 | 7 | 16 | 0 | 77 | 0 | 1.6 |
| Pt 25, ultra-thin, 0.5 μg $cm^{-2}$, deposited 20°C | 273 | 1.2 | 8 | 0 | 80 | 0 | 1.0 |

[a] n-H = *n*-hexane; 3-MP = 3-methylpentane; 2,3-DMB = 2,3-dimethylbutane; neo-H = neohexane; MCP = methylcyclopentane; CH = cyclohexane; B = benzene; CHe = cyclohexene.

TABLE 4

REACTION OF *n*-HEXANE OVER NICKEL FILM CATALYSTS: $C_6$ REACTION PRODUCTS[a]

| Type of catalyst and expt. no. | Reaction temp (°C) | $C_6$ reaction products (mole %) | | | | | Total conversion (%) | Selectivity |
|---|---|---|---|---|---|---|---|---|
| | | 2-MP | 3-MP | 2,3-DMB, neo-H, CHe | MCP | CH + B | | |
| Ni 1, ultra-thin film, 0.2 μg $cm^{-2}$, deposited 275°C | 273 | 11.6 | 26.6 | 0 | 0 | 61.8 | 0.6 | 0.12 |
| Ni 2, (111) film, ~0.1 mg $cm^{-2}$, deposited at 300°C | 273 | 10.5 | 10.5 | 0 | 0 | 79 | 8.6 | 0.005 |

[a] 2-MP = 2-methylpentane; 3-MP = 3-methylpentane; 2,3-DMB = 2,3-dimethylbutane; CHe = cyclohexene; neo-H = neohexane; MCP = methylcyclopentane; CH = cyclohexane; B = benzene.

TABLE 5

REACTION OF *n*-HEXANE OVER NICKEL FILM CATALYSTS: $C_1$–$C_5$ REACTION PRODUCTS[a]

| Type of catalyst and expt. no. | Reaction temp (°C) | $C_1$–$C_5$ reaction products (mole %) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | M | E | P | n-B | iso-B, neo-P | n-P | iso-P | CP |
| Ni 1, ultra-thin film, 0.2 μg cm$^{-2}$, deposited 275°C | 273 | 82.0 | 8.8 | 0.45 | 4.35 | 0 | 3.64 | 0.49 | 0.31 |
| Ni 2, (111) film, ~0.1 mg cm$^{-2}$, deposited 300°C | 273 | 98.2 | 1.20 | 0.037 | 0.36 | 0 | 0.24 | 0.016 | 0.005 |

[a] M = methane; E = ethane; P = propane; n-B = *n*-butane; iso-B = isobutane; n-P = *n*-pentane; iso-P = isopentane; CP = cyclopentane; neo-P = neopentane.

type). The average crystal size was in the region of 20 Å, with particles down to the limit of resolution (about 8 Å) also being apparent. Further details of the structure of ultra-thin films will be presented in a subsequent paper. It is useful at this stage to obtain a feeling for the film weights used in our ultra-thin films. Thus, for instance, if a monolayer of platinum atoms was close-packed on a plane surface with a nearest-neighbor distance equal to that in metallic platinum, 1 $cm^2$ of substrate would carry 0.49 $\mu g$ of platinum: the latter value is to be compared, for instance, with the ultra-thin platinum film weights of 0.25 to 1.0 $\mu g$ $cm^{-2}$ recorded in Table 1. In a similar way, the various ultra-thin nickel films we have used (Tables 4, 5) have film weights corresponding to about 50% of a close-packed nickel monolayer. In other words, the ultra-thin film catalysts contain an extremely small amount of metal, yet these films have catalytic activities of the same order of magnitude as thick films which expose a continuous metal surface. We emphasize, however, that we consider these ultra-thin films to consist, in the main, of very small crystals. For instance, if a platinum film of 0.5 $\mu g$ $cm^{-2}$ consisted entirely of crystallites of an average diameter of 20 Å, the average distance between the crystalline centers would be about 40–50 Å, a structure confirmed by electron microscopy.

In the absence of exact detailed knowledge about the distribution of crystal shapes in ultra-thin films, we shall base the discussion on the following proposals: (i) The average crystal size is about 20 Å (or less). (ii) The metal crystallites are of tetrahedral and/or octahedral shapes. One would expect the surface energy of the small crystallites to be minimized if the free surface consists entirely of (111) planes, and this is possible for tetrahedral and octahedral shapes. Furthermore, we note that Jaeger (private communication, CSIRO Division of Tribophysics) has observed the growth of tetrahedrally shaped nickel crystallites, each about 100 Å across, by vapor deposition on to a (111) silver substrate at 250°C.

### 1. *Reactions Over Platinum Films*

The first major point to note concerning the data in Table 1 is the much higher value of the selectivity factor for the reaction of *n*-hexane on ultra-thin platinum films, in the sense that hydrogenolysis is very much less important on ultra-thin films than on any of the thick films. The data in Table 2 confirm this because the proportion of methane in the $C_1$–$C_5$ products is lower on the ultra-thin films. The second point concerns the proportion of cyclic reaction products. As shown in Table 1 for the reaction of *n*-hexane, on ultra-thin films, cyclic reaction products make up at least 80% of the total $C_6$ products, and this is a markedly greater proportion than was obtained on any of the various types of thick films. The minimum proportion of carbocyclic products was, in fact, observed over a "fringe-free" film and was about 25%. It is clear from the irreproducible behavior of the "fringe-free" platinum films with *n*-hexane that we do not at present have the factors which govern their surface structure under complete control. Nevertheless, it is important to note that films of this type did, in fact, give the lowest proportion of carbocyclic reaction products. The two features of the reaction, the variation in the selectivity factor and in the proportion of cyclic reaction products, are in fact closely related.

However, the results show clearly that there exists a large difference in the propensity for cyclization of *n*-hexane and 2-methylpentane. On thick polycrystalline catalysts the proportion of methylcyclopentane formed from 2-methylpentane reached up to about 77%, while on an ultra-thin film the proportion was 80%. Thus, the reaction path of 2-methylpentane as estimated from the $C_6$ reaction products is virtually independent of film structure: in other words the cyclization process is apparently not demanding in terms of steric factors at the platinum surface. We shall return at a later section to possible reasons for this.

Because the reaction of *n*-hexane is

sterically demanding in the sense that the proportion of carbocyclic products is sensitive to film structure, the remaining comments in this section are based upon the behavior of this hydrocarbon.

It is of considerable interest to compare the reaction of *n*-hexane over ultra-thin and thick platinum films with the same reaction over 0.2% and 10% Pt on alumina catalysts (*10*). Thus over 0.2% Pt the proportion of methylcyclopentane in the $C_6$ reaction products was 25.6% compared with 7.2% over 10% Pt. It is likely that the platinum particle size is smaller in the 0.2% Pt than in the 10% Pt catalyst, so that although the actual proportions of methylcyclopentane are substantially smaller from the supported catalysts than from the film catalysts, the trends are the same in both systems, in that small particle size favors the formation of the cyclic product. This correspondence also extends to the selectivity factor which was rather less favorable towards hydrogenolysis on the 0.2% Pt catalyst (basing this comparison on the available data for reactions with 2- and 3-methylpentanes).

### 2. *Reactions Over Nickel Films*

Table 4 shows that over nickel film catalysts the selectivity factors are low, that is hydrogenation is the strongly favored reaction path. This is also confirmed in Table 4 which shows that methane is the dominant reaction product: this agrees with the known properties of nickel film catalysts (*7*).

Nevertheless, it is important to note from Table 4 that the selectivity factor for *n*-hexane reaction on an ultra-thin nickel film is substantially greater than on a (111) thick nickel film. That is, the propensity for the formation of $C_6$ reaction products is appreciably more important relative to hydrogenolysis on an ultra-thin film catalyst: again this difference is reflected in the proportions of methane in the $C_1$–$C_5$ products given in Table 5.

### 3. *Reaction Mechanisms*

We first deal with reactions over platinum. The skeletal isomerization of saturated hydrocarbons over various types of "normal" thick evaporated platinum films was demonstrated by Anderson *et al.* (*7*), with confirmation and extension in mechanistic detail by Anderson and Avery (*2*) and by Barron *et al.* (*8*), Corolleur (*10*), and Muller (*13*). The following discussion is based upon a knowledge of the mechanistic details obtained from a study of the reactions of molecules of varying sizes and structures (*2, 11*), and from the use of $^{13}C$-labeled molecules (*2, 10, 13*). It follows from this work, particularly from the studies by Corolleur (*10*) and Muller (*13*) with $^{13}C$-labeled hexanes, that in the isomerization reaction, *n*-hexane may pass through one of the following reaction paths:

1. a single C–C bond shift;
2. two consecutive C–C bond shifts;
3. a C–C bond shift followed by the formation of an adsorbed $C_5$ carbocyclic intermediate;
4. the formation of an adsorbed $C_5$ carbocyclic intermediate.

In all cases, isomerization may proceed from an adsorbed $C_5$ carbocyclic intermediate by reopening of the ring in a position other than that of closure, an isomerization mechanism emphasized by Gault and co-workers [Barron *et al.* (*8*)], while the C–C bond shift is the isomerization process discussed by Anderson and Avery (*2*). Furthermore, desorption of the adsorbed $C_5$ carbocyclic intermediate without ring opening leads to the formation of methylcyclopentane. Of course, in addition to these processes, the *n*-hexane molecule may form an adsorbed $C_6$ carbocyclic intermediate which may lead to cyclohexane or benzene on final desorption: the adsorbed $C_6$ carbocyclic intermediate may also be formed by ring enlargement by a C–C bond shift process from the adsorbed $C_5$ carbocyclic species, but this is probably a minor competitor to direct ring closure judging from the relatively small amount of cyclic $C_6$ products formed from 2-methylpentane (Table 3).

It is clear from this generalized isomerization mechanism that the products 2-

methylpentane and 3-methylpentane can be formed from *n*-hexane in various ways involving contributions from bond shift and adsorbed carbocyclic processes. However, it is worth noting that Corolleur (*10*) showed by the use of $^{13}C$-labeled reactant, that on a 0.2% Pt on alumina catalyst, the contribution of the process via an adsorbed $C_5$ carbocyclic intermediate was dominant, while on the 10% Pt catalyst both contributions were of comparable importance. Using the argument of platinum particle size to extrapolate to the behavior of films, we anticipate that the reaction over ultra-thin films will be dominated by the process via an adsorbed $C_5$ carbocyclic intermediate. Despite this expectation, it will be a matter of some importance to carry out this work with ultra-thin and with thick platinum films, because it will remove the existing ambiguity which is due to the unresolved problem of the effect of variable surface contamination with supported catalysts.* From the dependence of the extent of formation of carbocyclic reaction intermediate on film structure, we propose that the formation of a $C_5$ or $C_6$ carbocyclic reaction intermediate occurs preferentially at a crystallite corner site where there exists a platinum atom with a low coordination number.

For tetrahedral and octahedral crystallites, the corner atoms have three and four nearest neighbors, respectively, compared to nine nearest neighbors for an atom in a (111) surface. For a given crystallite shape the absolute number of corner atoms is constant, and the ratio $N_c/N_s$ of corner atoms to the total number of surface atoms falls rapidly as the crystal size increases (approximately as $l^{-2}$, where $l$ is a linear dimension of the crystal). The statistics of surface atoms on metal crystals of varying sizes and shapes has recently been summarized by Van Hardeveld and Hartog (*12*). For $N_c/N_s$ to exceed the modest value of 2%, the length of a crystal edge must be less than 12 and 10 atoms for tetrahedral and octahedral crystallites, respectively: that is, the overall size of each crystallite would have to be less than about 25 Å.

On this model, the irreproducible behavior of the "fringe-free" film catalysts must clearly be related to the degree of perfection of the film surface. Although the surfaces are substantially featureless when examined by replication/electron microscopic techniques, these techniques do not resolve the presence of surface features such as atoms in terrace edges or terrace kink positions, and the previous discussion of the likely structure of ultra-thin films suggests that only a quite small proportion of low-coordination platinum atoms is needed to have a dramatic effect on the product distribution. The data in Table 1 also shows that the reaction is insensitive to whether film catalysts of this type nominally expose (111) or (100) surfaces, probably because the effects of this difference are swamped by both surface imperfections and by the fringe regions.

In any case, however, ultra-thin films which favor the formation of adsorbed carbocyclic intermediates will therefore also favor the formation of $C_5$ and $C_6$ cyclic reaction products, in agreement with observation.

The fact that in the *n*-hexane reactions the selectivity factor is altered in favor of hydrogenolysis on going from an ultra-thin to a thick film with both platinum and nickel catalysts clearly implies that these two reaction paths involve different surface intermediates. Although the details of hydrogenolysis reactions are complex (*9*), one factor which is common to all such reactions appears to be the need for multiple adsorption of the carbon skeleton at not less than two catalyst sites. For instance, the 1–3 adsorption mode suggested by Anderson and Avery (*2*, *11*) for the C–C bond shift process in skeletal isomerization on platinum is also the likely intermediate for hydrogenolysis when this intermediate is attacked by surface hydrogen (*11*). Or again, on nickel hydrogenolysis probably requires at least 1–2 adsorption of the carbon skeleton (*9*, *16*) or the formation of even more extensively dehydrogenated species. In any case, it is clear that such

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* These experiments are planned in collaboration with Professor Gault.

intermediates will not be favored by surfaces which possess single low-coordinated metal atoms, in agreement with the observed trend in the selectivity factors.

It is instructive to compare our present results with those of Boudart *et al.* (*17*), who studied the reaction of neopentane over supported and powdered platinum catalysts. These workers measured the selectivity factor for isomerization versus hydrogenolysis and found that isomerization was favored by increasing the platinum particle size (measured by hydrogen chemisorption). There is no conflict between these and the present results: in fact, both results agree and are complementary within the general framework of hydrocarbon isomerization. The important point is that neopentane can isomerize by *only* a C–C bond shift mechanism: in other words, for both hydrogenolysis and isomerization of neopentane, the presence of low-coordinated corner platinum atoms is irrelevant. Boudart *et al.* (*17*) offered a reasonable explanation for the influence of particle size in terms of the relative importance for neopentane of the 1–3 diadsorbed mode and the triadsorbed mode, these two adsorption modes being the ones previously discussed by Anderson and Avery (*2*). Both the diadsorbed and the triadsorbed intermediates can lead to isomerization and to hydrogenolysis, but the relative importance of isomerization is substantially greater from the triadsorbed mode. The triadsorbed mode requires for its formation a triplet of platinum atoms such as occur on a (111) face or facet, and this will be favored by larger crystals, particularly those prepared by high temperature sintering.

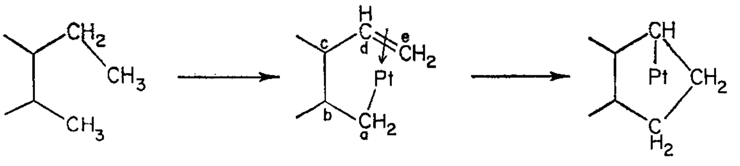
By considering both the results of the present work and those of Boudart *et al.* (*17*) it seems clear that the influence of platinum particle size and structure on the selectivity for hydrogenolysis versus isomerization and cyclization will, in general, be a complex one, because the result will be much dependent on hydrocarbon geometry, and one must examine each of the individual reaction paths separately. Those processes which depend on the formation of an adsorbed carbocyclic intermediate can be favored by small particles with a large proportion of corner atoms. However, with the comparative behavior of *n*-hexane and 2-methylpentane in mind, it must be clear that in some cases the propensity for cyclization, can be great enough to make its variation with catalyst structure of greatly reduced significance. Those isomerization reactions which proceed by C–C bond shift will be favored by a triadsorbed intermediate and thus favored by crystals with a large proportion of (111) facets. Of course, adsorption into this triadsorbed mode requires an isostructure in the molecule, and if this is not present then C–C bond shift can only occur via the 1–3 diadsorbed intermediate: the latter is less favorable for isomerization than the triadsorbed intermediate, and it does not demand a triplet of platinum atoms for its formation.

It should be noted that our discussion has so far only referred to the *relative* importance of hydrogenolysis versus isomerization and cyclization reactions. Work which uses supported or powdered catalysts to examine correlations between particle size and catalyst efficiency suffers from the difficulty due to the possible influence of a variable degree of surface contamination. This problem exists both for the measurement of specific reaction rates (rate per unit surface area of metal) and of catalyst specificity. In the case of the work by Boudart *et al.* (*17*), these workers were aware that their specific reaction rates were in some cases dependent on surface contamination, but since they showed that the catalyst specificity was independent of this factor, we consider that their correlation is genuine. The elimination of the difficulty due to variable surface contamination is a major factor in favor of the use of ultrathin and thick metal films for this type of work.

Other workers have noted an apparent correlation between the specific activity for hydrogenolysis and particle size. For instance, Carter *et al.* (*18*) noted that the specific activity of nickel/silica–alumina catalysts for ethane hydrogenolysis decreased by a factor of 20 as the relative particle size increased by a factor of 4 (due to sintering the catalyst in a hydrogen atmosphere). However, this system well illustrates the ambiguities inherent in working with supported catalysts, and the difficulties of disentangling real effects of particle size from effects due to changes in the degree of surface contamination (i.e., the chemical nature of the surface). Thus in the system studied by Carter *et al.*, the hydrogen adsorption isotherms measured at —78°C are markedly different in character to those for clean nickel: the isotherms for the supported nickel catalysts "saturate" in the region of 20–30 Torr which is a pressure greater by a factor of some $10^4$ than that needed for clean nickel. Moreover, the average metal particle sizes estimated by gas adsorption are greater by a factor of about five than the sizes estimated by X-ray line broadening. In addition, there is an apparent conflict with the results due to Yates *et al.* (*19*) who found that there was no dependence of the specific activity of a nickel/silica catalyst for ethane hydrogenolysis on apparent particle size measured by hydrogen adsorption. Another system to consider is the hydrogenolytic adsorption of propane on platinum black studied by McKee (*20*), where the specific activity increased with decreasing particle size due to sintering. In this case the particle size was measured by BET nitrogen adsorption, but the very low temperature (0°C) at which the platinum black was hydrogen-reduced before reaction would make it certain that the metal surface was not clean before reaction and there is again no way of knowing the extent to which the observed result was dependent on variations in the chemical composition of the surface. We believe, in short, that no convincing demonstration has yet been made of the dependence of hydrogenolysis specific activity on particle size *per se*, but an unambiguous result may be possible by the use of ultra-thin metal films. Such experiments are planned in this laboratory.

On the present model, a reaction path for *n*-hexane which involves, for instance, a bond shift followed by reaction via a carbocyclic intermediate in a single overall residence period, implies that the reactant molecule can be transferred between a reaction site on a crystal face and a single atom corner site. This transfer may occur via physically adsorbed reactant, or possibly by a migration of a chemisorbed molecule involving interconversions between species bound to the surface at one and then at two carbon atoms. In a multistep process such as this, involving transfer between different catalyst sites, the pore structure of a supported catalyst may be of great importance. For instance, if transfer between sites occurs via a physically adsorbed layer, this transport is competitive with desorption and the relative importance of these processes will depend on pore structure. This is analogous to the influence of pore structure on exchange kinetics recently discussed by Dwyer *et al.* (*21*). In any case, an effect of this type may well contribute to the variability in product distribution that can occur in the reaction of saturated hydrocarbons over platinum catalysts with varying types of (inert) supports (*10*), and it represents an effect which is additional to the influence of the variability in the surface structure of the platinum crystals.

A mechanism for ring closure at a catalyst site consisting of a single metal atom has been suggested by Sheppard and Rooney (*14*). This requires dehydrogenative adsorption to a precursor such as (I) This type of mechanism would be gen-

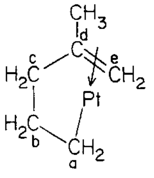


(1)

(I) (II)

erally applicable provided dehydrogenation to the formation of the C=C bond in (I) is possible. We propose from the present work that for a single Pt atom to function in this way, it should preferably be of low coordination in the metal lattice. As a minor variant to this mechanism, species II may be formulated as a $\pi$-allylic system in the ring and bound by a $\pi$-bond to the platinum atom [Barron *et al.* (*8*)].

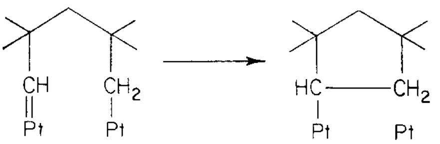
It remains to comment on why this type of specificity with regard to the coordination of the platinum atom is not apparent in the reactions of 2-methylpentane. We suggest that, if with 2-methylpentane ring closure involves a precursor analogous to (I), but with the methyl group carried on carbon atom d, that is



(III)

the effect of the methyl group will be to strengthen the dative bond from the C=C to the platinum, that is to make the formation of III possible in cases where the (high) coordination of the platinum atom would otherwise preclude its formation.

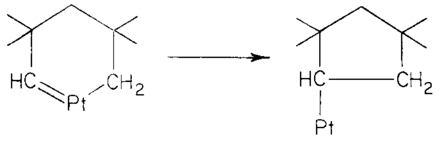
One further comment is required concerning the cyclization mechanism. Muller (*13*) has recently shown that the dehydrocyclization of 2,2,4,4-tetramethylpentane to 1,1,3,3-tetramethylcyclopentane occurs on "normal" thick polycrystalline platinum film catalysts with a rate that is comparable to the formation of 1,1,3-trimethylcyclopentane from 1,2,2-trimethylpentane. As Muller points out, a precursor of the type (I) cannot be formed from 2,2,4,4-tetramethylpentane, and it is clear that either reaction (1) is not correct, or at least there must be an alternative mechanism which is available. Muller suggests mechanism (2) which requires two adjacent platinum sites



(2)

(IV) (V)

Alternatively, it is of course possible to formulate this using only a single platinum atom



(3)

(VI) (VII)

If mechanism (2) is correct, it is to be expected that the cyclization of this reactant should not be favored by the use of ultrathin films, while the converse should be true if (3) is possible. We propose to check this point experimentally.

The reverse of the last step in reaction (1) can result in the opening of the ring in (II) in a position different from that in the precursor (I), and this would also be possible with species (IV) and (V) or with (VI) and (VII) in reactions (2) or (3), provided the new ring opening position was not sterically disallowed [as is the case with the particular structures used in reactions (2) and (3)]. The reverse of reactions (1), (2), or (3) cannot lead to ring opening adjacent to a quaternary carbon atom, and in fact hydrogenolytic ring opening with 1,1-dimethylcyclopentane on a platinum/carbon catalyst shows no propensity for ring opening adjacent to the quaternary carbon atom (cf. Newnham's (*15*) summary of Kazanskii's data).

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## REFERENCES

1. ANDERSON, J. R., AND MACDONALD, R. J., *J. Catal.* **13**, 345 (1969).
2. ANDERSON, J. R., AND AVERY, N. R., *J. Catal.* **5**, 446 (1966).
3. ANDERSON, J. R., AND MACDONALD, R. J., *J. Catal.* **19**, 227 (1970).
4. DIETZ, W. A., *J. Gas Chem.* **5**, 68 (1967).
5. *Amer. Petrol. Inst. Res. Proj.* **44**, Mass Spectral Data.
6. SANDERS, J. V., *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, ed.), Chapt. 1. Academic Press, London/New York, 1970, in press.
7. ANDERSON, J. R., AND BAKER, B. G., *Proc. Roy. Soc., Ser. A* **271**, 402 (1963). ANDERSON, J. R., AND AVERY, N. R., *J. Catal.* **2**, 542 (1963).
8. BARRON, Y., MAIRE, G., MULLER, J. M., AND GAULT, F. G., *J. Catal.* **5**, 428 (1966).
9. ANDERSON, J. R., AND BAKER, B. G., *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, ed.), Chapt. 7. Academic Press, London/New York, in press.
10. COROLLEUR, C., PhD thesis, University of Caen, 1969.
11. ANDERSON, J. R., AND AVERY, N. R., *J. Catal.* **7**, 315 (1967).
12. VAN HARDEVELD, R., AND HARTOG, F., *Surface Sci.* **15**, 189 (1969).
13. MULLER, J. M., PhD thesis, University of Caen, 1969.
14. SHEPPARD, F. E., AND ROONEY, J. J., *J. Catal.* **3**, 129 (1964).
15. NEWNHAM, J., *Chem. Rev.* **63**, 123 (1963).
16. KEMBALL, C., AND TAYLOR, H. S., *J. Amer. Chem. Soc.* **70**, 345 (1948).
17. BOUDART, M., ALDAG, A. W., PTAK, L. D., AND BENSON, J. E., *J. Catal.* **11**, 35 (1968).
18. CARTER, J. L., CUSUMANO, J. A. AND SINFELT, J. H., *J. Phys. Chem.* **70**, 2257 (1966).
19. YATES, D. J. C., TAYLOR, W. F., AND SINFELT, J. H., *J. Amer. Chem. Soc.* **86**, 2296 (1964).
20. MCKEE, D. W., *J. Phys. Chem.* **67**, 841 (1963).
21. DWYER, F. G., EAGLETON, L. C., WEI, J., AND ZEHNER, J. C., *Proc. Roy. Soc., Ser. A* **302**, 253 (1968).