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Reactions of Neopentane on Transition Metals

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Rates of hydrogenolysis, r_H, of neopentane have been measured on supported metal catalysts containing Ru, Rh, Pd, Os, Ir, Pt, and Au. At 250°C, values of r_H, referred to unit surface area of the metal, differ by 10 orders of magnitude, Au being the least active and Ru the most active metal investigated. The order of activity can be correlated with Pauling's percentage *d*-bond character.

Among all metals of Group VIII plus Cu and Au, only Ir, Pt, and Au are found to isomerize neopentane to isopentane. They do so with comparable selectivity. It is speculated that the exceptional ability of these three metals to isomerize neopentane is related to their high electronegativity and to a readily shifted surface valency as a result of promotion of *d* electrons to empty *s* levels.

INTRODUCTION

One of the recurrent problems of heterogeneous catalysis is the difference in activity between metals. Many important contributions to this problem have been made since the introduction 30 years ago by Beeck, Wheeler, Ritchie, and others of evaporated metallic films as experimental catalysts. However, these films can be used only at low temperatures and they cannot be regenerated.

Following Beeck's work, Schuit and Van Reijen showed that supported metal catalysts could be used, at least under specified conditions, as reliably as evaporated films for certain reactions (*1*). More recently, investigations in several laboratories have sanctioned the use of supported metals in fundamental studies of the activity of metals although the parasitic effect of supports must always be guarded against in each particular case (*2*).

Such a favorable case is the isomerization of neopentane to isopentane, a reaction discovered by Anderson and Avery (*3*) who showed that it took place on evaporated films of platinum and only on platinum among the metals investigated. The same reaction was then studied in our laboratory on platinum catalysts supported on alumina, silica, and carbon as well as on platinum powders (*4*).

We found that *selectivity*, defined as the ratio of specific rates of isomerization and hydrogenolysis, appeared to be structure sensitive. Following earlier suggestions by Anderson and Avery, this behavior was interpreted by the possibility of two modes of adsorption of neopentane on platinum: in a triadsorbed state, in particular, hydrogenolysis would take place at a lower rate than in a diadsorbed state. Hence, the rate of hydrogenolysis and also selectivity would depend on the concentration of active centers capable of binding neopentane in the triadsorbed state. Thus the reaction can be called a *demanding* one.

Because of the demanding nature of the hydrogenolysis of neopentane, a systematic survey of the activity of this reaction on various metals does not appear to be recommended. By contrast, the hydrogenolysis of ethane was studied successfully in great detail by Sinfelt and Yates (*5*) over Group VIII metals.

The reason why we undertook a survey of the reactions of neopentane on various metals was not a matter of activity. Rather

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the question was one of specificity: are other metals besides platinum capable of isomerizing neopentane? Anderson and Avery did not find any. More recently, Muller and Gault reported that 1,1,3-trimethylcyclopentane reacts to give xylenes selectively only on platinum evaporated films (*6*). Other metals tried by these authors were Fe, Co, Ni, Rh, and Pd. The selective reaction of 1,1,3-trimethylcyclopentane to xylenes appears closely related to the isomerization of neopentane and probably takes place through a similar surface intermediate.

In the present paper, we report results of a survey of all Group VIII metals, plus copper and gold. The first question was: *is platinum unique in its ability to isomerize neopentane?* As the work developed, because of very large differences in rates of hydrogenolysis of neopentane observed on various metals, a comparison of the activity of these metals became imperative, in spite of the demanding nature of the reaction.

EXPERIMENTAL METHODS

The recycle batch reactor with chromatographic analysis was described previously (*4*). Initial rates of hydrogenolysis and isomerization were measured under differential reactor conditions of approximately 0.02% conversion per pass and a total conversion of less than 2.0%. All runs were performed at a total pressure of 1 atm and a hydrogen:neopentane ratio of 10:1. A typical run is shown in Fig. 1.

Phillips research grade neopentane was purified by three pump–freeze–thaw cycles and stored in a liquid nitrogen bath. Cylinder hydrogen (99.95%) was purified by diffusion through a Milton Roy palladium thimble.

The catalysts on which quantitative data were obtained are listed in Table 1. Use was also made, for qualitative information, of the following supported catalysts: 10% Fe/SiO_2; 10% Co/SiO_2; 4.3% Ni/Al_2O_3; 10% Cu/SiO_2; 5% Cu/MgO.

The Os (*7*), Ir (*5*), and Rh (*8*) catalysts were prepared at Esso Research and Engineering Company as described in the respective references. The Fe, Co, and Ru catalysts were also prepared at Esso, but the method of preparation was not given. The Pd catalyst was prepared at Heraeus; the method of preparation was not given. The Au powder with a purity of 99.99% was obtained from Engelhard Industries. The Pt catalyst was described previously (*4*). The Cu/SiO_2 catalyst was prepared in this laboratory by impregnation of Cabosil with reagent grade $Cu(NO_3)_2 \cdot 3H_2O$ in doubly distilled water. The Cu/MgO catalyst was described previously (*9*). The Ni catalyst was a commercial catalyst.

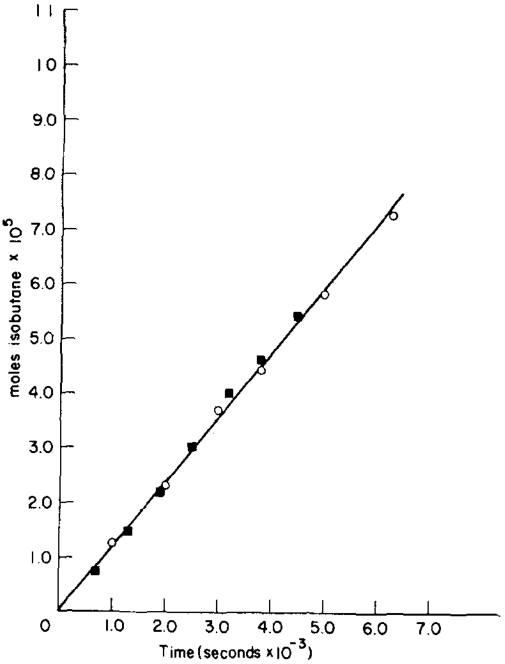

FIG. 1. A typical run at 180°C, total pressure 1 atm., H_2; hydrocarbon = 10:1; on a 5% Rh/SiO_2 catalyst: ●, Run 2B-2; ■, Run 2B-3; catalyst regenerated in flowing H_2 for 1 hr at 270°C.

With the exception of Os, Ru, Pt, and Au, pretreatment consisted of drying the catalyst in air at 100°C for 10 hr before weighing, outgassing at 10^{-2} torr at 150°C for 3 hr, and reducing in flowing hydrogen (70 ml/min) for 2 hr at 450°C. The Os and Ru catalysts were dried in a dessicator prior to weighing because of the possibility of forming toxic oxides at higher temperatures and were outgassed at 100°C for 3 hr. The Pt and Au catalysts were treated for 10 hr in hydrogen at 500°C.

The method for obtaining reproducible activity varied from catalyst to catalyst.

TABLE 1

Kinetic Data for the Hydrogenolysis and Isomerization of Neopentane

Metal	Wt (%)	Support	Metal surface area (m^2/g of catalyst)	E for hydrogenolysis (kcal/mole)	$\text{Log}_{10}\, r_0$ for hydrogenolysis (mole/m^2 sec)	E for isomerization (kcal/mole)	$\text{Log}_{10}\, r_0$ for isomerization (mole/m^2 sec)
Os	10	SiO_2	14.1[a]	32	8.6	—	—
Ir	10	SiO_2	18.6[a]	46	13	50	14
Pt	1.0	Spheron	0.31[b]	59	13	49	11
Au	100	—	0.058[c]	51	6.0	48	5
Ru	5.0	SiO_2	7.6[a]	36	10	—	—
Rh	5.0	SiO_2	11.9[a]	53	17	—	—
Pd	2.0	SiO_2	1.5[d]	—	—	—	—

[a] Determined by H_2 and CO chemisorption at Esso Research and Engineering Company.

[b] Determined by H_2, O_2 titration method in this laboratory.

[c] Determined by krypton BET adsorption in this laboratory.

[d] Determined by CO chemisorption at Heraeus.

For Rh, it was found that a 1-hr treatment in flowing hydrogen (70 ml/min) at 270°C after each run was sufficient to maintain an activity reproducible to within 10%. For Ir, 1 hr under flowing hydrogen at 450°C sufficed. For Os and Ru, constant activity could be maintained by treating the catalysts with flowing hydrogen at 150°C for 1 hr between runs. The Au catalyst was treated initially at 500°C for 10 hr and between runs was treated in flowing hydrogen for 2 hr at 500°C. The method of utilization of the Pt catalyst was described elsewhere (*4*).

Results

In all cases, the initial detected products were isopentane and isobutane. Methane peaks could not be measured because they coincided with the hydrogen peak. The specific activities for the hydrogenolysis at 250°C and isomerization at 307°C of neopentane are shown in Fig. 3. Except for the hydrogenolysis on Pd, these values were extrapolated by means of the Arrhenius plots shown on Fig. 2. From these plots, activation energies E are extracted and collected in Table 1 together with r_0 values defined by the relation $r = r_0 \exp(-E/RT)$. For Pt, we show a range of values for the rate of hydrogenolysis corresponding to those reported earlier (*4*), all extrapolated to 250°C by means of the activation energy reported in Table 1 and measured on one of the Pt catalysts investigated previously.

The only catalysts found to isomerize neopentane were, in decreasing order of activity, Ir, Pt, and Au. The positive result with Ir is striking because Anderson and Avery reported that Ir films were inactive for the isomerization of neopentane (*3*). However, in agreement with their results, we found Ir to be much more active than Pt for hydrogenolysis. This explains why Anderson and Avery missed isopentane among the products. We succeeded in finding it because of the higher sensitivity of our analytical apparatus.

In order to make the study complete, single experiments were performed with supported Fe, Co, Ni, and Cu catalysts: no trace of isomerization was observed, with any of the catalysts, at 312, 207, 178, and 309° respectively, although ample hydrogenolysis activity was observed in each case.

For the metals with which no isopentane was observed, we cannot say, without further work, that no isopentane was made. It could be that it was destroyed by hydrogenolysis very rapidly. But it must be noted that even as little as 0.1% conversion of neopentane to isopentane could have been detected readily. Such a low hypothetical conversion would have corresponded to a

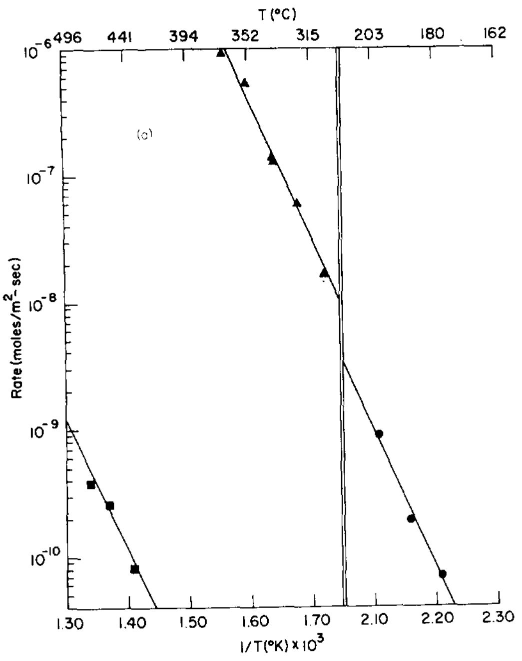

FIG. 2a. Arrhenius plots for extrapolation of kinetic data to a common temperature; isomerization: ▲, 1% Pt/Spheron; ●, 10% Ir/SiO_2; ■, Au powder.

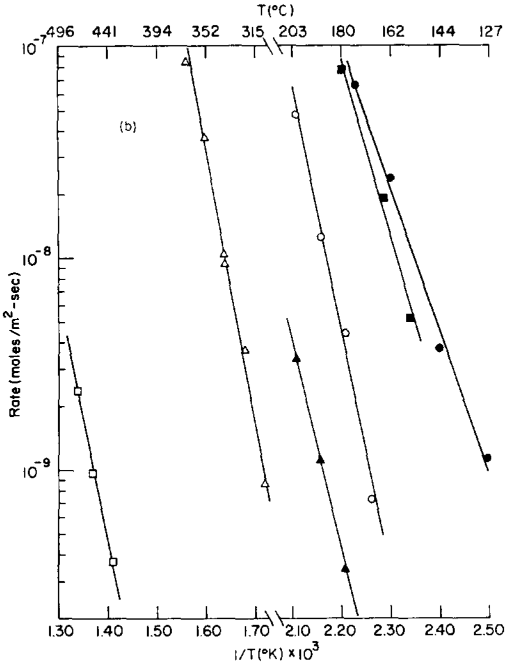

FIG. 2b. Arrhenius plots for extrapolation of kinetic data to a common temperature; hydrogenolysis: ●, 10% Os/SiO_2; ■, 5% Ru/SiO_2; ○, 5% Rh/SiO_2; ▲, 10% Ir/SiO_2; △, 1% Pt/Spheron; □, Au powder. (Data for Pt: taken from A. W. Aldag, Ph.D. dissertation, Stanford University, 1967.)

rate of isomerization about 10^{-3} times smaller than the rate of hydrogenolysis. We shall summarize results by saying that on Fe, Co, Ni, Cu, Ru, Rd, Pd, and Os, selectivity to isomerization was very small while it was of the order of unity for Ir, Pt, and Au.*

DISCUSSION

There have been many attempts in the past to account for the order of activity of transition metals acting as catalysts in a given reaction. One of them, first proposed 20 years ago by one of us (*10*) makes use of Pauling's percentage *d*-bond character, δ, of the metal. Correlations between δ and the catalytic activity of metals have proved successful in a number of cases, such as that of the hydrogenolysis of ethane (*5*). More recently, Yates and Sinfelt (*11*) pointed out that r_H, the rate of hydrogenolysis of ethane referred to unit surface area of the metal, passes through a maximum at Os in the series Re, Os, Ir, Pt. This also is the trend obtained by Pauling for values of δ in the same series, with a maximum value of δ for Os.

It must be noted that other parameters that can be used to correlate catalytic activities of metals, such as the electron per atom ratio (*12*) or an effective surface valency (*13*) do not exhibit this maximum at Os in the series from Re to Pt but rather decrease steadily as one progresses in the series. Thus we too prefer to correlate our values of r_H for neopentane with δ. As shown on Fig. 3, the correlation between r_H, and δ is only fair. As discussed in the introduction, a very good correlation between r_H and *any* parameter characteristic of the metal was not expected because of the demanding nature of the reaction which for a given metal can shift values of r_H by an order of magnitude, at least for platinum, as a result of catalyst pretreatment (*4*). It is nevertheless remarkable that the

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* *Footnote added in proof.* Further extensive work has now been completed which makes this statement quantitative. This work will be published separately.

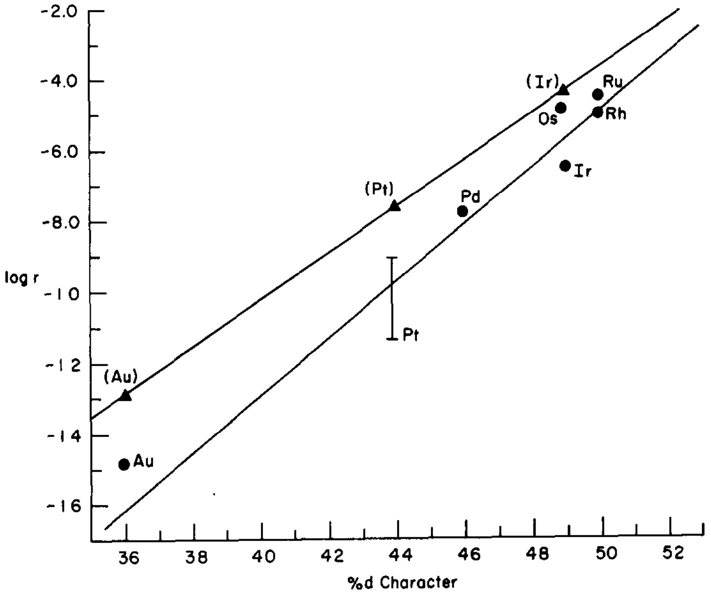

FIG. 3. Correlation of rates with Pauling's percentage *d*-bond character; ▲, isomerization at 307°C; ●, hydrogenolysis at 250°C.

order of values of δ parallels that of r_H over 10 orders of magnitude in the rate. The correlation between δ and r_I, the rate of isomerization of neopentane referred to unit surface area of the metal, is much better, as shown also on Fig. 3 and accounts for a variation of r_I over 8 orders of magnitude.

However, the main result of this work is not a matter of activity or selectivity. It is one of specificity: why are Ir, Pt, and Au the only three metals among the 11 investigated capable of isomerizing neopentane selectively? We shall now attempt to answer this question, in a speculative way, starting from the mechanistic ideas of Anderson and Avery (*14*).

These authors have proposed that in order for isomerization of aliphatic hydrocarbons to occur on Pt, the hydrocarbon must be 1,3-diadsorbed with one sp^2 carbon forming a double bond with a surface atom (structure A, Fig. 4). Isomerization then occurs through the intermediacy of B. They further suggest from Hückel MO calculations, that the greater the extent of electron transfer from the sp^2 carbon to the metal, the more energetically favorable isomerization becomes. This is because the adsorbed hydrocarbon then acquires the character of a carbonium ion. In this connection, it is interesting to note that neopentane can be isomerized at low temperature in Olah's extremely strong FSO_3H–SbF_5 "magic acid" (*15, 16*).

Two requirements thus seem necessary to obtain a "magic metal" capable of isomerizing neopentane. First its surface atoms must be sufficiently electronegative. Second, the surface valence of the metal must be able to shift readily from one value to another value in the rearrangement depicted in Fig. 4. The latter is also a requirement in the mechanism proposed by Gault although there are some differences

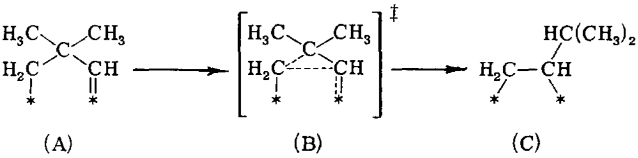

FIG. 4. Anderson and Avery's mechanism of isomerization of neopentane.

in detail between the nature of the intermediates postulated by the French (*6*) and the Australian (*14*) workers. In both cases, at least one carbon atom should change its hybridization state during the skeletal rearrangement and hence, the metal atom should also shift its valency.

Electronegativity of the metal atom appears to be a necessary but not sufficient condition for isomerization. Thus, on Pauling's scale, the electronegativity EN is 1.8 for Fe, Co, and Ni; 1.5 for Cu; and 2.2 for all six other Group VIII elements; and 2.4 for gold. On the basis of these values of EN, we could perhaps account for the lack of activity displayed by Fe, Co, Ni, and Cu, as well as for the isomerizing activity of gold but there is no way to account for the priviledged position of Ir and Pt among the six metals with a common value of EN equal to 2.2.

We suggest that the additional feature of a variable surface valency restricted to Ir, Pt, and Au can be found in recent work of Rhodin and co-workers (*13, 17*). The first part of the work deals with low energy electron diffraction (LEED) of gold. In fact, the admittedly weak reason why we tried gold as a catalyst for isomerization of neopentane was the reported LEED surface rearrangements of clean Pt (*18, 19*) and Au (*20–22*) crystals exposing their (100) face. These rearrangements have not been observed with other metals thus far, and in particular, they have not been seen with Pd and Ag which might be expected to behave very much like Pt and Au, respectively.

With respect to the reconstructed surfaces of gold observed with LEED, Palmberg and Rhodin argue that they may be ascribed to a particular sensitivity of the effective valency of that metal to the nature and number of neighboring atoms (*23*). In turn, this sensitivity is ascribed to the fact that the electronic configuration $5d^{10}6s^1$ of atomic gold can be readily promoted to an excited state of higher valency $5d^9 6s^2$ with the modest expenditure of only 1.1 eV. This energy is much higher for Ag, namely 2.7 eV. With Pt, promotion of the ground zero-valent atomic state $5d^{10}6s^0$ to other states of higher valency must also occur readily, according to Palmberg and Rhodin.

Further evidence for this postulated behavior of Pt was presented by Plummer and Rhodin in an investigation by means of field ion microscopy (FIM) of the binding energy of various individual metallic elements adsorbed on a W single crystal tip (*13*). For all the metal elements surveyed in their work (Hf, Ta, Re, Os, Ir, Pt, Au), they found that the measured values of the binding energy can be correlated and normalized by means of surface valence number which is the same for a given element on the various planes of W although this number varies of course from element to element with a maximum value of six at Re. However, for Pt and Ir, they found it necessary to postulate *two* values of this surface valence number depending on the surface environment. Plummer and Rhodin adapted the fundamental ideas of Pauling's theory of metals to explain their findings in terms of a variable surface valency for Pt and Ir.

Clearly then, the three metals Ir, Pt, and Au appear exceptional in their capacity to exhibit a variable valency at the surface, as suggested by their anomalous behavior in the FIM and LEED work of Rhodin, Somorjai, Gjostein, and others.

As a result of the present work, we like to speculate on the possibility that the isomerization of neopentane or related reactions are a suitable chemical probe of the dependence of surface valency on the atomistic nature of surface environment as stressed by Rhodin's school. Palmberg and Rhodin admit that it is somewhat surprising that Cu does not exhibit the rearranged LEED patterns of Au since Cu and Au are very much alike from the viewpoint of both electronic structure of the atom or of the band structure. They conclude that only those metals which are *extremely* sensitive to the nature of their environment, will show rearrangements of the type observed with Au. It must be noted again that, in this work, we found Cu to be totally inactive in the isomerization of neopentane. This may be again related to the less marked ability of Cu to shift its surface valency although the lower EN value of

Cu may well also account, at least in part, for its lack of reactivity in the Anderson reaction.

Conclusion

A few years ago, skeletal rearrangements of saturated hydrocarbons on metal surfaces were unknown. With the discovery by Anderson, Gault and Csicsery (*24*), of rearrangements taking place on metals without assistance from the support, this situation has been altered completely. In fact, the results of this work suggest that these rearrangements may well become sensitive chemical probes that will provide us with detailed information on surface valency for metals. Further developments of Pauling's original ideas following the lines of Rhodin's work and their application in catalysis by metals now appear very hopeful. In particular, it now appears possible to characterize surface valency of metals not only by Pauling's value of δ but by more subtle characteristics exhibited in striking parallelism by FIM, LEED, and catalytic work.

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