JOURNAL OF CATALYSIS **118**, 390–399 (1989)

Carbon-13 Isotopic Tracer Study of 2-Methylpentane Isomerization on PtTe/Al$_2$O$_3$ and PtSb/Al$_2$O$_3$ Catalysts

CHI H. CHENG AND GEOFFREY L. PRICE[1]

Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803

Received December 28, 1988; revised February 23, 1989

The mechanism of the isomerization reaction of 2-methylpentane on highly dispersed Pt/Al$_2$O$_3$ modified by the addition of Te or Sb has been investigated. The relative contributions of C$_5$-cyclic and bond shift mechanisms were determined by the use of 2-methylpentane (2-^{13}C) and 2-methylpentane (5-^{13}C) along with ^{13}C NMR analysis. *n*-Hexane was formed primarily by a C$_5$-cyclic mechanism while 3-methylpentane was produced by both cyclic and bond shift mechanisms. Isomerization via bond shift increases when Te or Sb is added to Pt/Al$_2$O$_3$. The results can be best described if the Rooney–Samman isomerization mechanism, which includes a transient cyclopropyl species as an intermediate in the methyl shift process, is favored upon Pt modification by Te or Sb. © 1989 Academic Press, Inc.

INTRODUCTION

The reaction of paraffins on metal surfaces has been the subject of many investigations and of particular interest are carbon skeletal isomerization reactions in which the isomers are produced on metal sites via several possible pathways. These pathways are generally categorized into C$_5$-cyclic and bond shift mechanisms (*1–4*). Possible reactive surface species related to these pathways have been reviewed by Gault (*5*). For the C$_5$-cyclic mechanism, the isomers are formed by carbon–carbon bond hydrogenolysis within a C$_5$-cyclic surface intermediate. For the bond shift mechanism, simple carbon–carbon bond displacements of the reactant molecules result in the formation of the isomerization products.

The relative importance of these two mechanisms can be determined by carbon-13 isotopic tracer techniques which have been performed extensively by Gault and his co-workers (*6–8*). Corolleur *et al.* (*6*) showed the dependence of these two mechanisms on metal crystallite size by studying the isomerization reactions of 2-methylpentane to 3-methylpentane and *n*-hexane using two Pt/Al$_2$O$_3$ catalysts with high and low platinum dispersion (0.2 and 10 wt% Pt). The C$_5$-cyclic mechanism is prominent on highly dispersed Pt/Al$_2$O$_3$, while bond shift mechanisms are more important on the 10 wt% Pt/Al$_2$O$_3$ catalyst. Similar studies using other reactants over several catalytic systems have also been reported (*7, 8*).

The use of bimetallic reforming catalysts in petroleum refining processes over the last two decades has attracted many researchers to investigate the effects of the second metal component on the platinum function. O'Cinneide and Gault (*9*) investigated isomerization in the C$_6$ system over Pt–Au-supported catalysts containing 10 wt% Pt and found that PtAu/Al$_2$O$_3$ resembles highly dispersed Pt/Al$_2$O$_3$ (0.2 wt% Pt) in both catalytic selectivity and mechanism. Diaz *et al.* (*10*) have investigated the 2-methylpentane isomerization reaction on PtRu/Al$_2$O$_3$ (10 wt% Pt, Pt/Ru atomic ratio = 2.4). They observed a small contribution of the cyclic mechanism for the production of 3-methylpentane compared with Pt/Al$_2$O$_3$. In addition, the researchers discovered that the bimetallic catalyst can pro-

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[1] To whom correspondence should be addressed.

0021-9517/89 $3.00

mote isomerization at a lower temperature, 493 K, and that methyl shift, which is never observed on Pt/Al_2O_3, is roughly one to two times more favorable than propyl shift. On a highly diluted $PtAu/Al_2O_3$ surface, Van Schaik *et al.* (*11*) have suggested that the bond shift mechanism becomes prominent.

Recently, Cheng *et al.* (*12, 13*) studied $PtTe/Al_2O_3$ and $PtSb/Al_2O_3$ catalysts and found that effects associated with the addition of a small amount of tellurium to Pt/Al_2O_3 can be described as a electronic modification of platinum, whereas $PtTe/Al_2O_3$ of high tellurium content and $PtSb/Al_2O_3$ are described better by geometric considerations. Thus, the elucidation of the effects of tellurium and antimony modifiers on the skeletal isomerization properties of platinum in terms of electronic and geometric effects are reported in this paper.

Earlier studies (*6–8*) determining the contribution of cyclic and bond shift mechanisms for C_6 isomerization reactions have normally been performed by studying the reactions of 2-methylpentane (2-^{13}C) and 2-methylpentane (4-^{13}C) and the product distribution of the ^{13}C-labeled species has been determined by analyzing the mass spectral fragmentation pattern of the products. Slight modifications have been made in this work where 2-methylpentane (5-^{13}C) was substituted for 2-methylpentane (4-^{13}C) because the reagents required to make the 5-^{13}C compound were more readily available and because there is little difference in the ultimate information which can be extracted from the data. Also, Fourier transform ^{13}C NMR was used for analytical purposes and this procedure shows clear advantages over the mass spectral methods previously reported. Interpretation of NMR spectra is much simpler yielding an increase in certainty in the relative proportions of products. Also, labeled reference compounds are not required for calibration. A disadvantage of the NMR technique, however, is that it requires a much larger sample.

EXPERIMENTAL

1. *Materials*

The catalysts, Pt/Al_2O_3, $PtTe/Al_2O_3$ (Te/Pt atomic ratio = 0.06, Pt = 1 wt%), and $PtSb/Al_2O_3$ (Sb/Pt = 0.97, Pt = 1.1 wt%), prepared by (co)impregnation methods were identical to those used in a previous paper (*12*). Briefly, Pt/Al_2O_3 was prepared from $H_2PtCl_6 \cdot 6H_2O$ impregnated on the Al_2O_3 support, and $PtTe/Al_2O_3$ was prepared from a solution of $H_2PtCl_2 \cdot 6H_2O$ and $H_2TeO_6 \cdot 2H_2O$, while $PtSb/Al_2O_3$ was prepared from a solution of $H_2PtCl_6 \cdot 6H_2O$ and $SbCl_3$. The catalyst was rinsed thoroughly with ammonia to remove the chlorine from the support and the efficiency of the procedure has been demonstrated by chlorine analysis of typical catalysts by X-ray fluorescence. Blank runs have been performed to demonstrate that the support is relatively inactive under the reaction conditions with both paraffins and olefins. These catalysts differ from industrial-grade catalysts in that most of the acidity has been purposely excluded so that reactions are primarily due to the Pt function.

Labeled 2-methylpentane (2-^{13}C) and 2-methylpentane (5-^{13}C) were prepared by first making the corresponding alcohols via Grignard syntheses followed by dehydration and hydrogenation using Al_2O_3 at 493 K and Pt/Al_2O_3 at 393 K, respectively. Similar procedures for the syntheses of the alcohols starting with $(CH_3)_2^{13}CO$ and $^{13}CH_3I$ have been described elsewhere (*6, 8*) and detailed experimental procedures and apparatus have also been described (*13*).

2. *Reaction and Sample Collection*

The catalyst pretreatment and reaction procedures were conducted in the usual manner in the recirculation batch system described previously (*12, 13*). Briefly, 50 mg (Pt/Al_2O_3) or 200 mg ($PtTe/Al_2O_3$ and $PtSb/Al_2O_3$) of catalyst was pretreated with 57.8 kPa H_2 at 673 K for at least 12 hr prior to reaction. The reactants consisted of 2.6–3.3 kPa (about 60 mg) of 2-methylpentane,

H_2/HC mole ratio = 17, and He to 107 kPa. The hydrocarbon products were collected at 78 K in a glass bulb after 5 to 15% conversion of 2-methylpentane and separated by preparative scale GC with a 10.7-m 9.5-mm-o.d. copper column (35 ft, ⅜ in.) packed with 4% SE-30 and 8% Carbowax 1540 on Chromosorb maintained at 315 K. For the 2-methylpentane (2-^{13}C) reaction, the entire C_6 hydrocarbon fraction, including 2-methylpentane, 3-methylpentane, *n*-hexane, and methylcyclopentane, was recovered in the prep-GC procedure and transferred to an NMR tube containing $CDCl_3$. However, for the 2-methylpentane (5-^{13}C) reaction, *n*-hexane and methylcyclopentane were separated from 2-methylpentane and 3-methylpentane and analyzed individually since the chemical shift corresponding to the 2 position in *n*-hexane could not be resolved from the 5 position of 2-methylpentane. Fractions other than C_6 were discarded.

3. *Fourier Transform ^{13}C NMR*

All experiments were run at 50.32 MHz on a Bruker WP-200 FT NMR spectrometer at room temperature. A 5-mm carbon-13 probe was used for all samples.

All spectra obtained were routine ^{13}C with proton decoupling. A standard sweep width of 220 ppm was used. In order for the ^{13}C spectra to be integrated accurately, an inverse gated proton decoupling technique was used. In this experiment, the proton decoupler was switched off during the relaxation delay which was set to 3 min per scan, approximately five times the longest spin–lattice relaxation, as determined by a separate inversion recovery experiment. The proton decoupler was switched on only during the data acquisition. The ^{13}C concentration of most samples was high enough such that suitable spectra could be obtained in 1–3 hr (20–60 scans).

The location of the ^{13}C in the hydrocarbon molecule was identified by matching the chemical shift to reference spectra from *The Sadtler Standard Spectra for ^{13}C NMR* (*14*). Naturally abundant ^{13}C in the product molecules was neglected since it exists only in 1/100 of the ^{13}C-enriched molecule.

RESULTS

1. *Product Distribution Data for the 2-Methylpentane Reaction*

Table 1 provides the product distribution data for the 2-methylpentane reaction on Pt/Al_2O_3, $PtTe/Al_2O_3$ (Te/Pt = 0.06), and $PtSb/Al_2O_3$ (Sb/Pt = 0.97). The data were taken at low conversion to ensure that secondary reactions had not occurred and this was also evident in the absence of extensive cracking, which would lead to the formation of *n*-butane and higher C_1/C_5 and C_2/C_4 ratios. No major effects were found on the selectivity toward hydrocracking products by the addition of Te or Sb. However, the Sb- and Te-containing catalysts exhibit lower *n*-C_6/3-MP ratios than Pt/Al_2O_3.

2. *Carbon-13 NMR Spectrum Interpretation*

The possible "tagged" species present in the reaction products of the labeled 2-methylpentane isomerization, according to

TABLE 1

Comparison of Product Distribution Data for 2-Methylpentane Reaction on Pt/Al_2O_3, $PtTe/Al_2O_3$, and $PtSb/Al_2O_3$

	Pt/Al_2O_3	$PtTe/Al_2O_3$[a]	Pt/Al_2O_3	$PtSb/Al_2O_3$[b]
Temp. (K)	563	563	613	613
% Conv.	11.10	8.32	11.37	11.91
C1	5.41	5.53	2.90	2.29
C2	4.41	4.93	1.85	2.61
C3	6.22	6.97	4.66	3.96
i-C4	9.10	9.01	3.60	5.22
n-C4	0.00	0.00	0.00	0.00
i-C5	12.52	13.10	7.13	5.64
n-C5	13.51	14.06	5.98	5.72
ΣC1–C5	51.17	53.60	26.12	25.44
MCP	8.56	11.30	23.57	23.76
3-MP	19.01	18.63	25.42	31.99
n-C6	21.26	16.47	24.89	18.81

[a] Te/Pt atomic ratio = 0.06.

[b] Sb/Pt atomic ratio = 0.97.

[c] The reported values are mole percent of 2-methylpentane converted to products, normalized to 100%.

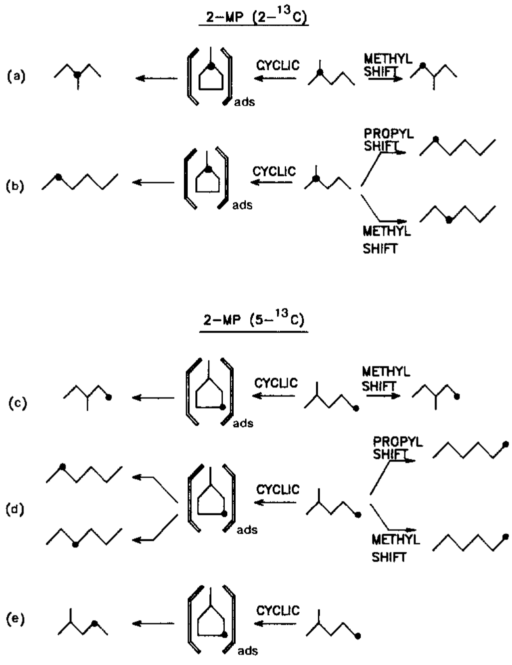


FIG. 1. Cyclic and bond shift mechanisms for the reactions of 2-methylpentane (2-^{13}C) and 2-methylpentane (5-^{13}C).

bond shift and C_5-cyclic mechanisms, are illustrated in Fig. 1.

Table 2 lists and identifies the chemical shifts of the reaction products, including 2-methylpentane, 3-methylpentane, *n*-hexane, and methylcyclopentane, for 2-methylpentane (2-^{13}C) isomerization on Pt/Al_2O_3 at 563 K. A typical spectrum is given in Fig. 2. The natural occurrence of ^{13}C in positions 1, 3, 4, and 5 of the unreacted 2-methylpentane (2-^{13}C) molecules appeared in the spectra in levels very close to the known natural abundance of ^{13}C and therefore are not products of the reactions. ^{13}C spin–spin splitting, which is usually not observed for naturally abundant ^{13}C atoms in ^{13}C NMR spectra, was found for naturally abundant ^{13}C next to the enriched ^{13}C atom in 2-methylpentane (2-^{13}C). The enriched ^{13}C in the 2 position of 2-methylpentane also experiences spin–spin splitting by all neighboring naturally abundant ^{13}C atoms, resulting in a complex multiplet with a very intense main line and several satellites (some lines are not completely resolved). The satellites represent areas consistent with the natural abundance of ^{13}C and are grouped with the main band. Enriched ^{13}C positions in the products of the reaction, 3-methylpentane, *n*-hexane, and methylcyclopentane, are exclusively those predicted according to the C_5-cyclic and bond shift mechanisms. The absence of other products indicates that secondary reactions or other rearrangements not predicted by bond shift or C_5-cyclic routes have not occurred. It should be mentioned that, in some spectra, the resonance of the 2 position of *n*-hexane was not well resolved from the 1 position of 2-methylpentane, but this did not upset our studies, since *n*-hexane (2-^{13}C) was the only *n*-hexane species observed. *n*-Hexane (3-^{13}C), expected from methyl shift, was not detected in any experiment. Therefore, the production of *n*-hexane (2-^{13}C) can be attributed totally to propyl shift and C_5-cyclic mechanisms (see Fig. 1b).

TABLE 2

Chemical Shifts of Products from 2-Methylpentane (2-^{13}C) Isomerization on Pt/Al_2O_3 at 563 K

Position (ppm)	Assignment	Area
14.26[c] 14.34[c]	2-MP (5-^{13}C)	0.95
20.51[c]	2-MP (4-^{13}C)	1.01
22.24[c] 22.94[c]	2-MP (1-^{13}C)	1.85
22.73	*n*-C6 (2-^{13}C)	1.78
27.40[a] 27.43[a] 27.76[b] 28.09[a] 28.13[a]	2-MP (2-^{13}C)	101.33
29.15	3-MP (2-^{13}C)	0.41
34.61	MCP (1-^{13}C)	1.31
36.19	3-MP (3-^{13}C)	1.03
41.12[c] 41.81[c]	2-MP (3-^{13}C)	0.99

[a] Satellite peak due to spin–spin splitting.
[b] Main band.
[c] Naturally abundant ^{13}C in 2-MP (2-^{13}C) reactant.

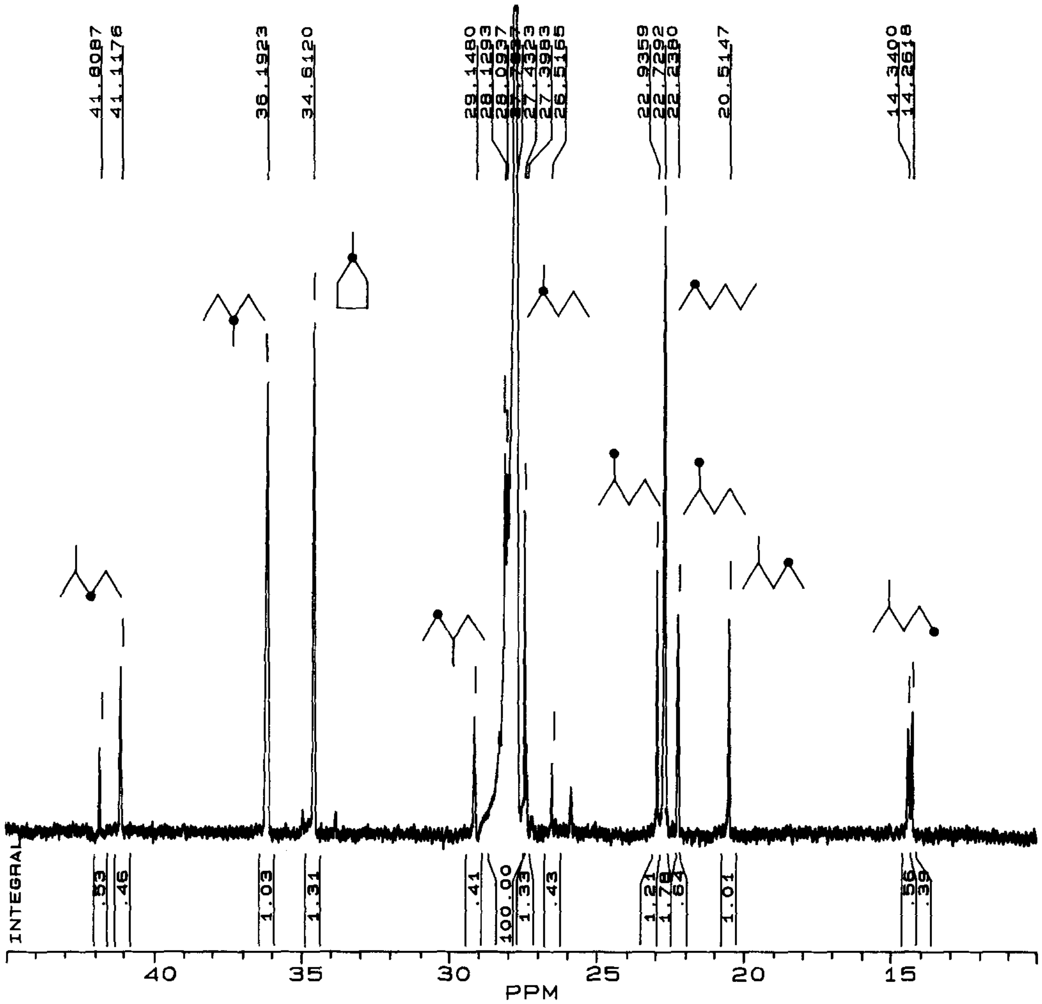


FIG. 2. Typical ^{13}C NMR spectrum of reaction products from 2-methylpentane (2-^{13}C) isomerization.

For the 2-methylpentane (5-^{13}C) reaction, the products were separated into two groups, 2-methylpentane + 3-methylpentane and *n*-hexane + methylcyclopentane, which were analyzed individually. The results for a typical spectrum of the former are presented in Table 3. The relative areas of the bands corresponding to ^{13}C in positions 1, 2, and 3 of 2-methylpentane are again in close agreement with those calculated on the basis of the natural abundance of ^{13}C and therefore, these species are not formed via catalytic reactions. The spectrum also shows a triplet which was assigned to 2-methylpentane (4-^{13}C). The two satellite peaks appearing at 20.15 and 20.84 ppm are caused by ^{13}C spin–spin splitting of the naturally abundant ^{13}C at position 4 by the enriched neighboring ^{13}C in position 5, as expected. The central peak at 20.48 ppm is ascribed to the 2-methylpentane (4-^{13}C) product from the ring opening of the cyclic intermediate, methylcyclopentane (3-^{13}C). 3-Methylpentane (1-^{13}C), produced from both cyclic and bond shift mechanisms, was also detected, but, since both mechanisms give this product, it bears no direct information on the relative rates of C_5-cyclic to bond shift mechanisms.

The chemical shifts observed for the *n*-

TABLE 3

Chemical Shifts of Products from 2-Methylpentane ($5\text{-}^{13}C$) Isomerization on $PtTe/Al_2O_3$ at 563 K

Position (ppm)	Assignment	Area
	Sample 1	
11.43	3-MP ($1\text{-}^{13}C$)	0.34
14.32[a] 14.62[b]	2-MP ($5\text{-}^{13}C$)	10.86
20.15[c] 20.84[c]	2-MP ($4\text{-}^{13}C$)	0.10
20.48	2-MP ($4\text{-}^{13}C$)	0.26
22.61[c]	2-MP ($1\text{-}^{13}C$)	0.21
27.68[c] 27.74[c]	2-MP ($2\text{-}^{13}C$)	0.10
41.39[c]	2-MP ($3\text{-}^{13}C$)	0.11
	Sample 2	
22.67	*n*-C6 ($2\text{-}^{13}C$)	2.93
25.29	MCP ($3\text{-}^{13}C$)	3.28
31.60	*n*-C6 ($3\text{-}^{13}C$)	2.61

[a] Satellite peak due to spin–spin splitting.

[b] Main band.

[c] Naturally abundant ^{13}C in 2-MP ($5\text{-}^{13}C$) reactant.

hexane and methylcyclopentane group from the isomerization of 2-methylpentane ($5\text{-}^{13}C$) are also given in Table 3. It is evident that the C_5-cyclic mechanism is operative as indicated by the formation of methylcyclopentane ($3\text{-}^{13}C$) (see Fig. 1). Surprisingly, no *n*-hexane ($1\text{-}^{13}C$), expected via bond shift of 2-methylpentane ($5\text{-}^{13}C$), was observed in three of the four experiments. Only a small amount was observed in the fourth experiment (Pt/Al_2O_3 at 613 K). The peaks at 22.67 and 31.60 ppm were identified as *n*-hexane ($2\text{-}^{13}C$) and *n*-hexane ($3\text{-}^{13}C$), respectively, and must be produced by ring opening of methylcyclopentane.

The contribution of C_5-cyclic and bond shift mechanisms for the conversion of 2-methylpentane to 3-methylpentane were determined directly by the relative areas of the 3 and 2 positions of 3-methylpentane (Fig. 1a).

For the conversion of 2-methylpentane to *n*-hexane, it is necessary to couple the results from the reactions of 2-methylpentane ($2\text{-}^{13}C$) and 2-methylpentane ($5\text{-}^{13}C$) in order to evaluate the relative contributions of C_5-cyclic and methyl and propyl shift mechanisms. For 2-methylpentane ($5\text{-}^{13}C$), the ratio of C_5-cyclic to the "total" bond shift (see Fig. 1d) is

$$\frac{\text{cyclic mech.}}{\text{propyl shift} + \text{methyl shift}} = \frac{n\text{-}C_6(2\text{-}^{13}C) + n\text{-}C_6(3\text{-}^{13}C)}{n\text{-}C_6(1\text{-}^{13}C)}.$$

This ratio is then used in the analysis of data obtained with 2-methylpentane ($2\text{-}^{13}C$). *n*-Hexane ($2\text{-}^{13}C$) can be produced from both C_5-cyclic and bond shift mechanisms from 2-methylpentane ($2\text{-}^{13}C$) (Fig. 1b). The fraction of *n*-hexane ($2\text{-}^{13}C$) produced by the C_5-cyclic mechanism is calculated from the ratio obtained from the 2-methylpentane ($5\text{-}^{13}C$) reaction. The remaining *n*-hexane ($2\text{-}^{13}C$) corresponds to propyl shift while the *n*-hexane ($3\text{-}^{13}C$) corresponds to methyl shift.

3. *Relative Contributions of Cyclic and Bond Shift Mechanisms*

The relative importance of C_5-cyclic and bond shift mechanisms for the isomerization of 2-methylpentane to 3-methylpentane and *n*-hexane using Pt/Al_2O_3, $PtTe/Al_2O_3$ ($Te/Pt = 0.06$), and $PtSb/Al_2O_3$ ($Sb/Pt = 0.97$) was determined by these procedures and the results are summarized in Tables 4 and 5.

The C_5-cyclic mechanism accounted for more than 70% of the conversion of 2-methylpentane to 3-methylpentane on Pt/Al_2O_3 at both 563 and 613 K. This is in agreement with other studies using highly dispersed Pt/Al_2O_3 catalysts (*6*) under similar conditions. However, the relative importance of the C_5-cyclic mechanism declines significantly with the addition of tellurium or antimony to Pt/Al_2O_3. These results are similar to those obtained using $PtRu/Al_2O_3$ (*10*), but is contrary to those using $PtAu/Al_2O_3$ (*9*).

TABLE 4

Product Distribution of Isotopic Species for the Isomerization Reactions of 2-Methylpentane (2-^{13}C) and 2-Methylpentane (5-^{13}C) on Pt/Al_2O_3, $PtTe/Al_2O_3$, and $PtSb/Al_2O_3$[a]

Catalyst	Reactant	T (K)	3-MP (3-^{13}C)	3-MP (2-^{13}C)	n-C6 (1-^{13}C)	n-C6 (2-^{13}C)	n-C6 (3-^{13}C)
Pt/Al_2O_3	2-MP (2-^{13}C)	563	71.5	28.5	0	100	0
	2-MP (5-^{13}C)	563	[b]	[b]	0	52.7	47.3
$PtTe/Al_2O_3$	2-MP (2-^{13}C)	563	64.4	35.6	0	100	0
	2-MP (5-^{13}C)	613	[b]	[b]	0	52.9	47.1
Pt/Al_2O_3	2-MP (2-^{13}C)	613	71.9	28.1	0	100	0
	2-MP (5-^{13}C)	613	[b]	[b]	9.3	44.3	46.4
$PtSb/Al_2O_3$	2-MP (2-^{13}C)	613	39.7	60.3	0	100	0
	2-MP (5-^{13}C)	613	[b]	[b]	0	60.0	40.0

[a] Naturally abundant ^{13}C in the labeled reactant has been removed.

[b] Not predicted from cyclic or bond shift reactions and none observed.

The C_5-cyclic mechanism is almost totally responsible for the formation of n-hexane from 2-methylpentane on all the catalysts tested. Methyl shift was not found and only 9% propyl shift was detected using Pt/Al_2O_3 at 613 K. The predominance of the C_5-cyclic mechanism over bond shift mechanisms for the conversion of 2-methylpentane to n-hexane has been observed on $PtAu/Al_2O_3$ and $PtRu/Al_2O_3$ bimetallic systems as well as on highly dispersed Pt/Al_2O_3 catalysts (*6*). The ring opening of methylcyclopentane (3-^{13}C) (formed from the 2-methylpentane (5-^{13}C) reaction) yielding n-hexane (2-^{13}C) and n-hexane (3-^{13}C) of equal amounts is expected. The discrepancy in these amounts for $PtSb/Al_2O_3$ is probably due to a sample of low concentration in n-hexane.

The selectivities for the breakage of the two secondary–secondary and one secondary–tertiary carbon bonds in the methylcyclopentane intermediate have not been obtained in this work due to the experimental difficulties in quantitatively transferring all of the C_6 hydrocarbon components into the NMR tube while maintaining-high purity preparative GC cuts.

DISCUSSION

Earlier exploratory studies on platinum-catalyzed isomerization emphasized mainly the dependence on the metal particle size and the results were therefore explained more or less on the basis of geometric crystallographic considerations. Examples of these are the work done by Corolleur *et al.* (*6*), O'Cinneide and Gault (*9*), and Diaz *et al.* (*10*). These authors compared poorly dispersed Pt/Al_2O_3 (loaded with at least 10 wt% Pt and composed of large metal crystallites) with alloy catalysts such as $PtRu/Al_2O_3$ and $PtAu/Al_2O_3$, or with highly dispersed Pt/Al_2O_3 (0.2 wt% Pt). In this work, the Pt/Al_2O_3 catalysts employed are already highly dispersed. The relative contributions of C_5-cyclic and bond shift mechanisms for the conversion of 2-methyl-

TABLE 5

Contribution of C_5-Cyclic and Bond Shift Mechanisms for the Isomerization Reactions of 2-Methylpentane on Pt/Al_2O_3, $PtTe/Al_2O_3$, and $PtSb/Al_2O_3$

Catalysts	T (K)	2-MP to 3-MP		2-MP to n-C6		
		C M[a]	M S[b]	C M[a]	P S[c]	M S[b]
Pt/Al_2O_3	563	71.5	28.5	100	0	0
$PtTe/Al_2O_3$	563	64.4	35.6	100	0	0
Pt/Al_2O_3	613	71.9	28.1	90.7	9.3	0
$PtSb/Al_2O_3$	613	39.9	60.3	100	0	0

[a] C_5-cyclic mechanism.

[b] Methyl shift.

[c] Propyl shift.

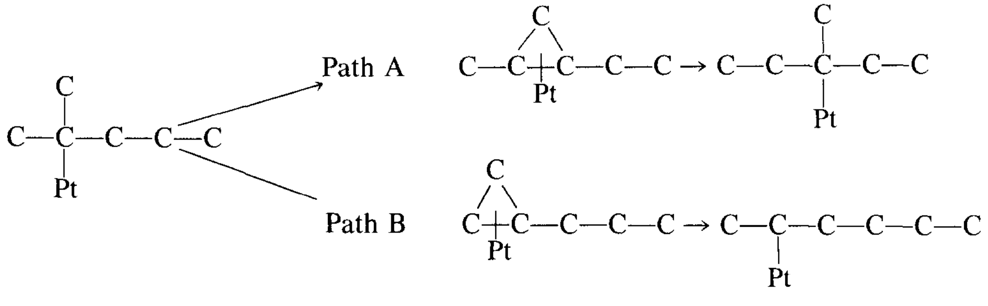
pentane to 3-methylpentane and *n*-hexane obtained on our catalysts are also in good agreement with those reported in the literature for a highly dispersed Pt/Al_2O_3 catalyst (*6, 9*).

The platinum function in $PtTe/Al_2O_3$ (Te/Pt = 0.06) should remain highly dispersed since the small amount of tellurium causes only an electronic modification. For $PtSb/Al_2O_3$ (Sb/Pt = 0.97) catalysts, the platinum surface area has probably been greatly reduced by the antimony. Isotopic dilution experiments reported in a previous paper (*12*) also show a decrease in adsorbed CO dipole–dipole coupling when Sb is added to Pt/Al_2O_3, indicating that the mutual distance between active platinum sites has been increased, and these centers probably appear as rather isolated atoms. Many isomerization mechanisms requiring single or multiple continuous platinum sites have been proposed to explain platinum-catalyzed skeletal isomerization. Mechanisms requiring single carbon atom interaction with the surface are more appropriate in our systems since platinum centers are well dispersed. This is also consistent with our previous observations which indicates that the specific rate of isomerization is insensitive to geometric effects (*12*).

Reactive species with one and two platinum sites for C_5-cyclic isomerization have been reviewed by Gault (*5*). According to Gault, a selective C_5-cyclic mechanism, which predominates in catalysts with large platinum crystallites, does not allow interconversion between 2-methylpentane and *n*-hexane. Hence, a nonselective cyclic mechanism, which occurs only on highly dispersed catalysts (as in our catalysts), must be responsible for the formation of *n*-hexane from 2-methylpentane in our studies. 3-Methylpentane probably accompanies *n*-hexane through nonselective C_5-cyclic pathways though some may be formed through a selective C_5-cyclic pathway which operates in parallel if there is a distribution of surface sites.

Four basic bond shift mechanisms, the Anderson–Avery mechanism, the Muller–Gault mechanism, the Garin–Gault mechanism, and the Rooney–Samman mechanism, have been reviewed by Gault (*5*). The Anderson–Avery and Muller–Gault mechanisms are less likely to be operative in our systems since they require a larger number of platinum atoms for the isomerization to occur. Although the Garin–Gault mechanism requires only a single carbon atom interaction with a platinum site, it involves carbon–carbon bond breaking/making, and a concurrent increase in hydrocracking products associated with an increase in bond shift mechanism after alloying would probably be observed if the Garin–Gault mechanism is operative. However, our results show that after the addition of tellurium or antimony to Pt/Al_2O_3, the selectivity for hydrocracking remains roughly constant. On the other hand, the isomerization mechanism of Rooney–Samman would not require an increase in hydrocracking activity concurrent with an increase in bond shift and therefore is more likely to be the predominant mechanism in both the tellurium and the antimony systems.

According to the Rooney–Samman mechanism (*15*), the isomerization of 2-methylpentane to 3-methylpentane and *n*-hexane via bond shift can be depicted as



The carbenium-ion-like transient species (*5*) in path A is probably much more stable than that in path B on the basis of thermodynamic viewpoints and the criteria for the stability of carbenium ions. Therefore, the yield to 3-methylpentane should be higher, in agreement with our findings. Catalysts with large platinum crystallites generally favor propyl shift over methyl shift in the formation of *n*-hexane from 2-methylpentane (*9*). In these systems, the Anderson–Avery mechanism and the Muller–Gault mechanism may be more important in promoting isomerization via bond shift. Note that the Rooney–Samman mechanism can promote only methyl shift isomerization. We have observed a small amount of propyl shift over Pt/Al_2O_3 at 613 K and this activity is destroyed by addition of antimony, again indicating platinum dilution effects. Diaz *et al.* (*10*) also found that methyl shift is more favorable than propyl shift upon alloying Pt/Al_2O_3 with ruthenium. No methyl shift has been observed in the formation of *n*-hexane from 2-methylpentane, indicating that path B in the Rooney–Samman mechanism is insignificant under our reaction conditions. Path A of the Rooney–Samman mechanism is clearly preferred over the C_5-cyclic mechanism in the isomerization of 2-methylpentane to 3-methylpentane when tellurium or antimony modifiers are added to Pt/Al_2O_3.

With these observations concerning C_5-cyclic and bond shift mechanisms in hand, the fundamental question is why the addition of tellurium or antimony to platinum increases the relative contribution of the bond shift mechanism (Table 5). The effect of tellurium on the bond strength of the chemisorbed species with the platinum sites is manifest. For the Rooney–Samman mechanism, the transient species is stabilized by lowering the energy of the antibonding orbital associated with one of the three-carbon-center orbitals in the transient species by interaction with the platinum *d*-orbitals (*15*). The platinum *d*-orbital is in turn modified by electronic donation from tellurium to platinum (*12*). Thus, we expect the observed electronic interaction to alter the rate of the isomerization reaction proceeding according to the Rooney–Samman mechanism. The nonselective C_5-cyclic mechanism does not depend on a similar intermediate and therefore, tellurium electronic interactions will not affect its rate to the same extent. A change in selectivity is therefore observed.

Since the nonselective C_5-cyclic mechanism and the Rooney–Samman bond shift mechanism require only single platinum atoms, the increase in the latter by alloying of platinum with antimony can hardly be explained by geometric (surface dilution) effects. However, if our Pt/Al_2O_3 catalysts contain some relatively large platinum crystallites which form 3-methylpentane via the selective C_5-cyclic mechanism, these sites could be destroyed by surface dilution resulting in a relative increase in the rate of bond shift. Another possibility is that a highly diluted Pt surface indeed favors the Rooney–Samman mechanism as other investigators have suggested (*11*), although a detailed explanation is not known.

CONCLUSIONS

Isomerization reactions of 2-methylpentane (2-^{13}C) and 2-methylpentane (5-^{13}C) show that C_5-cyclic and bond shift mechanisms can well describe the isomerization reactions of 2-methylpentane to 3-methylpentane and *n*-hexane. *n*-Hexane was formed primarily by a C_5-cyclic mechanism on the highly diluted platinum surface. C_5-cyclic and bond shift mechanisms are both responsible for the formation of 3-methylpentane, while the latter becomes more favorable after the addition of tellurium or antimony to Pt/Al_2O_3. The mechanism of isomerization is best described by the Rooney–Samman mechanism for bond shift and a nonselective C_5-ring opening for the cyclic mechanism.

ACKNOWLEDGMENTS

The authors thank Mr. Marcus Nauman in the Chemistry Department at LSU for ^{13}C NMR experiments and also express their appreciation to the Exxon Foundation for financial support. The assistance of Dr. Kenneth Riley at Exxon Research and Development in Baton Rouge, Louisiana, is especially appreciated.

REFERENCES

1. Anderson, J. R., and Avery, N. R., *J. Catal.* **5,** 446 (1966).
2. Barron, Y., Cornet, D., Maire, G., and Gault, F. G., *J. Catal.* **2,** 152 (1963).
3. Barron, Y., Maire, G., Muller, J. M., and Gault, F. G., *J. Catal.* **5,** 428 (1966).
4. Garin, F., and Gault, F. G., *J. Amer. Chem. Soc.* **97,** 4466 (1975).
5. Gault, F. G., "Advances in Catalysis," Vol. 33, p. 1. Academic Press, New York, 1981.
6. Corolleur, C., Corolleur, S., and Gault, F. G., *J. Catal.* **24,** 385 (1972).
7. Dartigues, J. M., Chembellan, A., and Gault, F. G., *J. Amer. Chem. Soc.* **98,** 856 (1976).
8. Chambellan, A., Dartigues, J. M., Corolleur, C., and Gault, F. G., *Nouv. J. Chim.* **1,** 1 (1977).
9. O'Cinneide, A., and Gault, F. G., *J. Catal.* **37,** 311 (1975).
10. Diaz, G., Garin, F., and Maire, G., *J. Catal.* **82,** 13 (1983).
11. Van Schaik, J. R. H., Dessing, R. P., and Ponec, V., *J. Catal.* **38,** 273 (1975).
12. Cheng, C. H., Dooley, K. M., and Price, G. L., *J. Catal.* **116,** 325 (1989).
13. Cheng, C. H., Ph.D. dissertation, Louisiana State University, 1988.
14. The Sadtler Standard Spectra, 100 MHz ^{13}C-NMR, Sadtler Research Laboratories (1969).
15. McKervey, M. A., *Rooney, J. J., Samman, N. G., J. Catal.* **30,** 330 (1973).