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Mechanism of the Bond-Shift Skeletal Isomerization of Alkanes over Pd, Ni, and Ni–Ag Catalysts: Evidence for Participation of Intermediate Carbenes

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The skeletal rearrangement reactions of butane, 2-methylpropane, and 2,2-dimethylpropane were investigated over Al_2O_3- and SiO_2-supported Pd, Pt, Ni, and Ag–Ni catalysts. As opposed to Pt, isomerization over the other catalysts proceeds mainly by carbene intermediates by a so-called "external C_1-migration" pathway. This reaction is parallel with homologation. Hydrogen sensitivities and radiotracer studies confirm these suggestions.

INTRODUCTION

Muller and Gault, interpreting the absence of isomer formation on Pd from 2,2-dimethylpropane (*1*), 2,2,4,4,-tetramethylpentane (*2*) and 1,1,3-trimethylcyclopentane (*2*) and considering the developments in the field of the olefin metathesis chemistry, have proposed a "carbene metathesis" mechanism of the bond shift rearrangement (*2*). In recent publications this interpretation of Muller and Gault has been extended to investigations performed with Pt catalysts (*3, 4*). The application of the carbene metathesis rearrangement to interpret the features of the isomerization on Pt has been strongly questioned by Ponec (*5*) and Rooney (*6*). In fact, homologation studies (*7–9*) have confirmed that Pt exhibits very poor chain lengthening and thus CH_2 formation activity in the temperature range used generally for isomerization studies ($T < 623$ K). It should be noted, however, that both Pd and Ni do promote chain lengthening homologation (*7–9*), and hence the original suggestion of Muller and Gault might not be entirely excluded on these metals. Clarke and Rooney have explained the mechanism of isomerization of small alkanes over Pd and Pt by the formation of a transient species of pseudocarbonium ion (*10c,a*). This conclusion has been strongly supported by experiments with caged hydrocarbons (*10*) and by deuterium labeling studies (*11, 12*). These independent investigations clearly show that a σ-alkyl surface species is sufficient for bond shift skeletal rearrangement. Small amounts of 2,3-dimethylbutane and benzene were formed from 2,2-dimethylbutane over Pd-black (*13*). Their opposite hydrogen sensitivity was interpreted in terms of both isomerization mechanisms occurring, the carbene one leading to aromatics and the pseudocarbenium one to saturated isomers.

Relatively few data are available for the isomerization of alkanes over Ni (*14, 15*) and the mechanism of the isomer formation as far as we know has not been discussed in detail.

The obvious discrepancies in the literature considering the mechanism of isomerization over Pd and the lack of information with Ni and Ni–Ag catalysts have prompted us to investigate and compare the isomerization and chain lengthening activity of these metals.

EXPERIMENTAL

The catalytic experiments have been performed in an all-glass static circulation sys-

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tem (0.1443 dm^3) attached to a gas chromatograph. The hydrocarbons were analyzed at 60°C with a 3-m-long column packed with 16 w/w% squalane. For a few additional measurements a 50-m-long capillary column with squalane was used. The formation of the hydrocarbons with higher carbon number than the parent compound and that of some cracking products was also monitored by a quadrupole mass spectrometer (QMS 511). The reactions were followed up to 20–30% conversion and the reaction rate was calculated from the slope of the product formation. Product selectivity has been determined from the rate data in conformity with previous definitions (*16, 17*); the rate of product formation was divided by the rate of the consumption of the parent compound.

The catalysts used have been prepared by conventional techniques. Ni/SiO_2 and $Ni-Ag/SiO_2$ catalysts were prepared by impregnation of SiO_2 (SAS) with nitrate salts (5.0 wt% metal) and decomposition in air followed by reduction (693 K, 5 h) in hydrogen. The alloying of the Ni clusters with Ag was indicated by the catalytic data themselves as well as by the decreasing irreversible chemisorption of *n*-hexane at 523 K.

The reduced $Ni-Ag/SiO_2$ samples with O-35 at.% Ag did not give X-ray diffraction lines of any metallic phase present; this indicates high metal dispersion. The dispersion of 5.0 wt% Ni/SiO_2 and 10 wt% Ni/SiO_2 has been inferred from H_2 chemisorption measurements. With the 65, 80, and 89 at.% Ag–Ni samples (5 wt% metal loading) the X-ray diffraction line broadening gave crystallite sizes of 5.5, 6.5, and 8.0 nm, respectively. Pd/SiO_2 and Pd/Al_2O_3 catalysts have been prepared by solution of $Pd(NH_3)_4Cl_2$; the support material used was SiO_2 (SAS Scientific Chemicals Ltd, 50–100 mesh) and γ-Al_2O_3 (Condea NG and SB). The number of surface Pd sites and the dispersion have been inferred from O_2 chemisorption data (*18*). The preparation of Pt-black and Pt/SiO_2 catalysts and their structural properties have already been described in detail (*19, 20*).

RESULTS AND DISCUSSION

Isomerization of *n*-butane (*n*-But), 2-methylpropane (2MPr), and 2,2-dimethylpropane (neopentane, neoP) has been investigated in the temperature range 400–583 K. The selectivity of isomer formation as well as that of chain lengthening measured under identical conditions are presented in Table 1. With the catalysts studied, 5 wt% Ni/SiO_2, 5 at.% $Ag-Ni/SiO_2$, 35 at.% $Ag-Ni/SiO_2$, 85 at.% $Ag-Ni/SiO_2$, 1 wt% Pd/γ-Al_2O_3(NG), and 0.123 wt% Pd/γ-Al_2O_3(SB), isomerization of 2,2-dimethylpropane was not observed. Another interesting observation is that the selectivity of isomer formation from *n*-butane exceeds that from 2-methylpropane over 5 wt% Ni/SiO_2, 5 at.% $Ag-Ni/SiO_2$, 85 at.% $Ag-Ni/SiO_2$, and 0.123 wt% Pd/γ-Al_2O_3(SB). It is obvious that over these catalysts the selectivity of isomerization does not follow the sequence (*1, 10*) 2,2-dimethylpropane > 2-methylpropane > *n*-butane which could be expected in the case of the formation of a transient species with pseudocarbonium ion character (*10*). With 35 at.% $Ag-Ni/SiO_2$ and 1 wt% Pd/γ-Al_2O_3(NG) samples the selectivity of isomerization of 2-methylpropane is commensurable with that of *n*-butane. According to the data of Anderson and Avery (*1*) on both oriented and unoriented Pt film the selectivity of isomerization of 2-methylpropane was higher than that of *n*-butane. As shown by data in Table 1 this observation remains valid even under our hydrogen-deficient conditions over a Pt-black.

The isomerization of *n*-butane and 2-methylpropane was accompanied by the formation of the next higher alkane. The mere occurrence of chain lengthening homologation, e.g., formation of *n*-pentane from *n*-butane, would not be sufficient to suggest that transient carbenes do participate in the formation of isomers. However,

TABLE 1

Transformation of *n*-Butane, 2-Methylpropane, and 2,2-Dimethylpropane over Pd, Ni, and Pt Catalysts. Selectivity of the Isomer Formation (S_{iso}) and That of Chain Lengthening (S^{n}_{hom} and S^{b}_{hom}, Normal and Branched Products, Respectively)

Experiment[a]	Catalyst	Hydrocarbon[b]	Selectivity × 100			$-R$[c] (mol s^{-1} g^{-1}_{Met})
			S_{iso}	S^{n}_{hom}	S^{b}_{hom}	
A	1 wt% Pd/γ-Al_2O_3 (NG)	*n*-But	8.74	4.06	7.67	8.01×10^{-6}
		2MPr	15.43	0.31	9.84	5.10×10^{-6}
		neoP	0.00	0.00	0.00	5.23×10^{-6}
B	0.123 wt% Pd/γ-Al_2O_3 (SB)	*n*-But	9.13	3.15	4.83	6.13×10^{-5}
		2MPr	8.77	0.19	4.49	5.07×10^{-5}
		neoP	0.00	0.00	0.00	5.32×10^{-5}
C	5 wt% Ni/SiO_2	*n*-But	7.18	2.55	4.24	2.01×10^{-5}
		2MPr	5.07	0.05	3.65	1.33×10^{-5}
		neoP	0.00	0.00	0.00	1.73×10^{-5}
D	5 at.% Ag–Ni/SiO_2	*n*-But	5.53	1.75	2.93	1.34×10^{-5}
		2MPr	4.42	0.05	1.37	7.95×10^{-6}
		neoP	0.00	0.00	0.00	1.10×10^{-5}
E	35 at.% Ag–Ni/SiO_2	*n*-But	10.17	3.42	6.51	5.86×10^{-7}
		2MPr	12.10	0.13	6.43	1.07×10^{-7}
		neoP	0.00	0.00	0.00	1.18×10^{-7}
F	85 at.% Ag–Ni/SiO_2	*n*-But	8.53	8.51	4.83	1.02×10^{-7}
		2MPr	6.15	0.08	2.13	9.31×10^{-8}
		neoP	0.00	0.00	0.00	9.88×10^{-8}
G	Pt-black	*n*-But	50.53	0.08	0.07	1.73×10^{-8}
		2MPr	84.31	0.00	0.03	2.13×10^{-8}
		neoP	85.12	0.00	0.00	1.10×10^{-8}
H	3 wt% Pt/SiO_2; $D = 80\%$	*n*-But	44.81	0.01	0.02	8.78×10^{-6}
		2MPr	89.43	0.00	0.01	2.71×10^{-6}
		neoP	73.51	0.00	0.00	1.03×10^{-5}
I	3 wt% Pt/SiO_2; $D = 80\%$	*n*-But	76.51	0.07	0.09	2.28×10^{-6}
		2MPr	94.31	0.01	0.08	3.33×10^{-6}
		neoP	72.92	0.00	0.00	2.37×10^{-6}

[a] Experiments E and H were measured with 1.33 kPa HC, $T = 565$ K. In experiment *E*, $p_{HC}/p_{H_2} = 0.3$; in experiment H, $p_{HC}/p_{H_2} = 0.22$. In experiments A–D, F, G, and I, $p_{HC} = 4$ kPa, $p_{HC}/p_{H_2} = 0.88$, $T = 565$ K.

[b] *n*-But, *n*-butane; 2MPr, 2-methylpropane; neoP, neopentane, 2,2-dimethylpropane.

[c] $-R$ signifies rate of consumption of parent compound.

the product distribution of the chain lengthening reaction shows that besides *n*-alkane (S^{n}_{hom}) a substantial amount of branched homolog (S^{b}_{hom}) appears in the reaction. This phenomenon was also observed with propane and 2-methylbutane (Table 2). Thus with *n*-butane, for example, the ratio 2-methylbutane/*n*-pentane is 1.66, 1.90, and 1.88 with 5 wt% Ni/SiO_2, 35 at.% Ag–Ni/SiO_2 and 1 wt% Pd/γ-Al_2O_3(NG), respectively. It would be tempting to argue that 2-methylbutane is formed by immediate isomerization of a chemisorbed *n*-pentane species. The experiments with 2-methylpropane show, however, that the reaction yields only a small amount of *n*-pentane besides 2-methylbutane. The 2-methylbutane/*n*-pentane ratio is observed to be 75.3 and 31.74 with 5 wt% Ni/SiO_2 and 1 wt% Pd/γ-Al_2O_3(NG), respectively. Similar observations were made with 2-methylbutane over 5 wt% Ni/SiO_2 and 1 wt% Pd/γ-Al_2O_3(NG) (Table 3).

The selective addition of carbenes to a β-

TABLE 2

The Selectivity of the Formation of 2-Methylpropane (S_{2MPr}), 2-Methylbutane (S_{2MBut}), and *n*-Pentane (S_{nP}) from *n*-Butane over Pd Catalysts (D = Dispersion)

Catalysts	p_{HC} (kPa)	p_{HC}/p_{H_2}	T (K)	Selectivity × 100 S_{2MPr}	S_{2MBut}	S_{nP}	$-R_{n\text{-But}}$[a] (mol g_{Pd}^{-1} s^{-1})
1 wt% Pd/SiO_2	4	0.88	533	7.01	17.2	6.5	1.42×10^{-5}
D = 17%	1.33	0.2	554	5.69	1.89	0.96	3.83×10^{-5}
	1.33	0.2	515	3.80	2.21	1.11	1.05×10^{-7}
1 wt% Pd/γ-Al_2O_3(NG)	1.33	0.2	558	8.92	1.35	0.787	1.27×10^{-5}
D = 8%	4	0.88	553	8.74	7.67	4.06	8.01×10^{-6}
	1.33	0.2	522	6.32	1.63	0.75	4.99×10^{-6}
	1.33	0.2	474	5.09	2.00	1.45	1.23×10^{-7}
0.123 wt% Pd/γ-Al_2O_3 (SB)	1.33	0.2	518	6.95	1.76	0.92	6.27×10^{-6}
D = 65%	1.33	0.2	552	8.03	1.25	0.65	4.18×10^{-5}
1 wt% Pd/γ-Al_2O_3 (SB)	1.33	0.2	504	3.22	2.79	1.14	1.78×10^{-6}
	1.33	0.2	552	7.52	1.45	0.73	1.74×10^{-5}

[a] Rate of consumption of *n*-butane.

carbon atom of *n*-alkanes has not been observed in the previous homologation studies over metal (*7–9*). Moreover, under these moderate conditions there is no significant difference between the homologation selectivity of *n*-butane and 2-methylpropane. Homologation of 2,2-dimethylpropane was not observed, in agreement with earlier data (*7–9*). Although it is beyond the scope of this paper to discuss these observations in detail, considering the reasons for the observed discrepancy the following explanations are suggested. (i) In the previous studies, by virtue of the high reaction temperature ($T > 593$ K) and the more effective carbon poisoning activity of larger alkanes (*n*-pentane, 2-methylpentane, and *n*-hexane), the metal surface

TABLE 3

Selectivity of the Transformation of Propane and that of 2-Methylbutane (2-MBut) over Pd and Ni Catalysts

Catalyst	p_{HC} (kPa)	p_{HC}/p_{H_2}	T (K)	Hydrocarbon	Selectivity × 100[a] iC_4	nC_4	nP	2M2B⁼	2MP	3MP	*n*-Hex	MCP	Benz	(mol s^{-1} g_{Met}^{-1})
5 wt%	1.33	5.1	553	2-MBut	25.59	31.53	4.02	4.06	1.02	0.24	—	—	0.74	8.87×10^{-6}
Ni/SiO_2	4.00	1.16	553	2-MBut	19.41	25.58	9.24	22.3	2.71	0.56	0.15	0.59	0.64	1.33×10^{-6}
1 wt%	2.66	2.67	524	2-MBut	41.64	43.48	2.67	0.37	1.28	0.77	0.078	0.087	—	4.76×10^{-6}
Pd/γ-Al_2O_3(NG)	4.00	1.18	553	2-MBut	38.96	40.93	7.46	12.2	5.06	3.55	0.17	0.078	—	9.12×10^{-6}
5 wt%	4.00	1.16	553	Propane	2.11	1.83	—	—	—	—	—	—	—	1.23×10^{-7}
Ni/SiO_2	1.33	5.3	553	Propane	0.03	0.02	—	—	—	—	—	—	—	3.41×10^{-7}
1 wt% Pd/γ-Al_2O_3(NG)	4.00	1.12	553	Propane	2.36	2.21	—	—	—	—	—	—	—	4.36×10^{-8}
0.123 wt% Pd/γ-Al_2O_3(SB)	4.00	1.13	557	Propane	1.78	1.63	—	—	—	—	—	—	—	8.46×10^{-8}

[a] Products isobutane(iC_4), *n*-butane (nC_4), *n*-pentane (nP), (2M2B⁼), 2-methylpentane (2MP), 3-methylpentane (3MP), *n*-hexane (*n*-Hex), methylcyclopentane (MCP), and benzene (Benz).

[b] Rate of consumption of the parent compound.

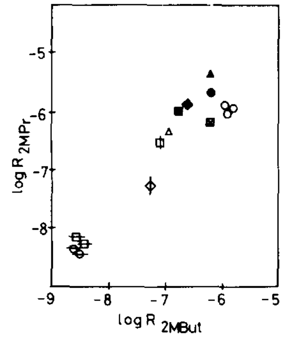


FIG. 1. Rate of 2-methylbutane (2MBut) formation as a function of 2-methylpropane (2MPr) formation from *n*-butane over Pd catalysts. ○, ⧫, and ⊖ were measured with 1 wt% Pd/SiO$_2$ (D = 17%): (○) p_{HC} = 4 kPa, p_{HC}/p_{H_2} = 0.88, T = 553 K; (⧫, ⊖) p_{HC} = 1.33 kPa, p_{HC}/p_{H_2} = 0.2, T = 554 and 515 K, respectively. ■, ⊠, and ⊟ were measured with 1 wt% Pd/γ-Al$_2$O$_3$(NG) (D = 8%): (⊠) p_{HC} = 4 kPa, p_{HC}/p_{H_2} = 0.88, T = 553 K; (■, ⊞, ⊟) p_{HC} = 1.33 kPa, p_{HC}/p_{H_2} = 0.2, T = 558, 522, and 474 K, respectively. △ and ▲ were measured with 0.123 wt% Pd/γ-Al$_2$O$_3$(SB) (D = 65%), p_{HC} = 1.33 kPa, p_{HC}/p_{H_2} = 0.2, T = 518 and 552 K, respectively. ◊ and ◆ were measured with 1 wt% Pd/γ-Al$_2$O$_3$(SB), p_{HC} = 1.33 kPa, p_{HC}/p_{H_2} = 0.2, T = 504 and 552 K, respectively.

was strongly poisoned by carbonaceous residues. The congestion of the active sites owing to a steric or an electronic factor might inhibit addition of carbenes on the substituted end of the double bond in alk-1-enes. (ii) One cannot rule out, on the other hand, that at elevated temperatures, simply owing to the effective rupture of the C–C bond between the primary and tertiary carbon atoms (*21*) and because of the ease of demethylation of toluene and xylenes, the real selectivity of carbene addition was obscured (*22*).

Returning to the problem of isomerization experiments, the reaction of *n*-butane on a group of Pd catalysts has indicated that 2-methylpropane always appears together with *n*-pentane and 2-methylbutane. This is clearly demonstrated in Fig. 1 where the rate of the 2-methylpropane formation (expressed in mol s^{-1} g$_{Pd}^{-1}$) is depicted as a function of 2-methylbutane formation. (Because of the variation of the metal loading and of the experimental conditions the rate of 2-

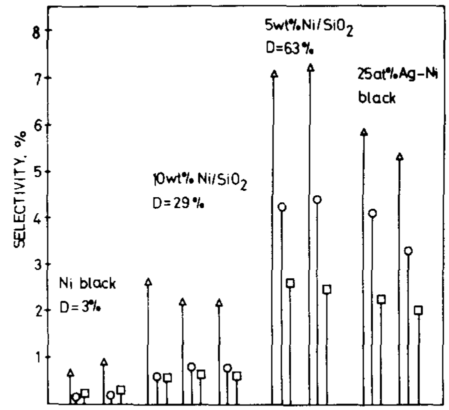


FIG. 2. The selectivity of isomerization and chain lengthening of *n*-butane (p_{HC} = 4 kPa, p_{HC}/p_{H_2} = 0.88, T = 553 K). (△, ○, □) Selectivity of formation of 2-methylpropane, 2-methylbutane, and *n*-pentane, respectively. The rate of *n*-butane consumption is 7.55 × 10^{-7}, 3.69 × 10^{-6}, 1.51 × 10^{-5}, and 3.44 × 10^{-9} mol s^{-1} g$_{Met}^{-1}$), in experiments denoted on abscissa as 12, 38, 63, and 107, respectively.

methylpropane formation spans more than 2.5 orders of magnitude.) The selectivity of the formation of 2-methylpropane (S_{2MPr}), *n*-pentane (S_{nP}), and 2-methylbutane (S_{2MB}) is presented in Table 2.

The results of experiments with Ni catalysts of different dispersion (D) and with a set of Ni–Ag bimetallic catalysts are presented in Figs. 2 and 3, respectively. These

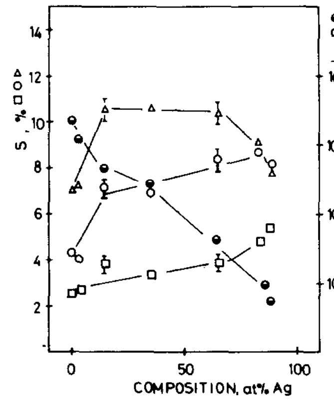


FIG. 3. The rate of *n*-butane consumption (●) in mol s^{-1} g$_{Met}^{-1}$ and the selectivity of the formation of 2-methylpropane (△), 2-methylbutane (○), and *n*-pentane (□) on Ag–Ni catalysts (T = 553 K, p_{HC} = 4 kPa, p_{HC}/p_{H_2} = 0.88).

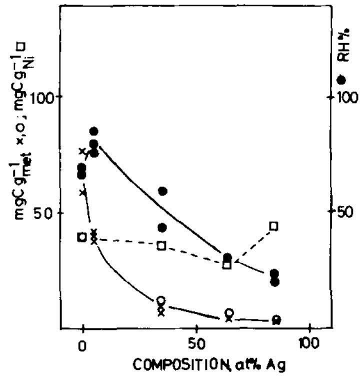


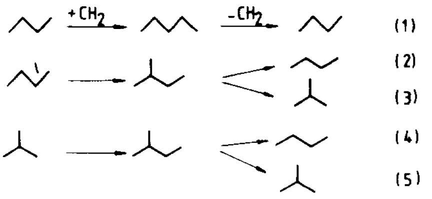
FIG. 4. Amount of the irreversibly bonded *n*-hexane (×) in mg C/g_{met} at 523 K (p_{HC} = 0.53 kPa) and the percentage of the fraction removable in 26.6 kPa H_2 at 523 K (●, RH%) and the carbon coverage of the working Ag–Ni catalyst (experimental conditions in Fig. 3) expressed in mg C/g_{met} (○) and in mg C/g_{Ni} (□) on Ag–Ni catalysts.

results confirm that the isomerization activity, just as with Pd samples, parallels the homologation activity. The high dispersion allowing localized metal–hydrocarbon interactions seems to favor both isomerization and homologation chain lengthening. With the Ag–Ni/SiO_2 catalysts the selectivity of isomerization and that of chain lengthening are observed to increase between 0 and 15 at.% Ag but decrease at 85 and 89 at.% Ag, respectively.

Alloying of Ni-black with 25 at.% Ag (the selectivities are given in Fig. 2) decreased the specific activity for the transformation of *n*-butane by a factor of 219. (The rate of *n*-butane consumption with Ni-black and 25 at.% Ag–Ni alloy was 7.55 × 10^{-7} and 3.44 × 10^{-9} mol s^{-1} g_{cat}^{-1} at 553 K and p_{HC} = 4 kPa, p_{HC}/p_{H_2} = 0.83. The BET surface areas were measured to be 5.2 and 6.6 m^2 g^{-1}, respectively). With the highly dispersed Ag–Ni/SiO_2 samples the rate of *n*-butane consumption decreased continuously to one-sixth of the activity of the Ni/SiO_2 sample in the composition range of 0 to 35 at.% Ag. The rate data themselves and the chemisorption measurements with *n*-hexane at 523 K (Fig. 4) and the amount of the surface carbon remaining on the surface after evacuation of the reaction mixture (Fig. 4) seem to confirm that Ni and Ni–Ag ensembles coexist on the SiO_2 surface in a broad Ag–Ni composition range. The results concerning the activity of the Ag–Ni-black and Ag–Ni/SiO_2 samples can be convincingly interpreted by a dispersion-influenced surface segregation. Examples showing that the surface composition is a function of the particle size have already been observed with Pt–Au (*23*), Pt–Cu, and Rh–Ag (*24*) alloys.

Inspection of the experimental results with Pd, Ni, and Ag–Ni catalysts provides evidence that in the course of isomerization of alkanes one should consider the formation and reaction of intermediate carbenes. In interpreting the mechanism of the skeletal rearrangement, say with *n*-butane, one might tentatively suggest that 2-methylpropane is formed by recombination of a propene species with a CH_2 unit e.g., by the mechanism of Muller and Gault (*2*). The investigations with propane (Table 2) seem to support this assumption since both *n*-butane and 2-methylpropane appeared in commensurable quantity. This reaction route, however, although it is attractive, might not be important because with 2,2-dimethylpropane the continuous formation of 2-methylpentane along with 2-methylpropane was not observed although this latter hydrocarbon was abundant over Pd catalysts (S_{2MPr} = 0.7–0.95). It is more likely therefore that the isomerization is initiated by the chain lengthening of the starting hydrocarbon and the isomer is formed from the C_{n+1} product by the rupture of a terminal methyl group. Accepting this proposal, 2-methylbutane, as shown in Scheme 1, is a common intermediate of the isomerization of both *n*-butane and 2-methylpropane. (Reactions 1, 2, and 5 can lead only to the scrambling of the carbon atoms.) The results in Table 2 confirm that there is an almost equal chance for the formation of *n*-butane and that of 2-methylpropane from 2-methylbutane.

In the following we discuss the results of



SCHEME 1. Formation of isomers from *n*-butane and 2-methylpropane by carbene insertion methyl abstraction mechanism.

this work and we look for evidence in support of an "external C_1 migration" mechanism.

(i) 2-Methylbutane, once formed from either *n*-butane or 2-methylpropane by chain lengthening, might undergo subsequent reaction on the surface since its desorption is likely to be hindered to a larger extent than that of chemisorbed *n*-butane or 2-methylpropane. For this reason there is a chance for the removal of a terminal carbon atom. The hindrance of intermediate product desorption has already been observed in hydrogenolysis and chain lengthening reactions over Ni catalysts (*22, 25, 26*). This phenomenon may explain why the selectivity of isomerization of *n*-butane increased while that of chain lengthening decreased with increasing temperature on a group of Pd catalysts (see results in Table 2).

(ii) The investigations with Pt catalysts (*16, 27*) have shown that the optimum hydrogen pressure for the bond shift skeletal isomerization can be observed at higher pressures than that for C–C bond rupture. With a 65 at.% Ag–Ni catalyst this feature of the bond shift reaction could not be observed since the selectivity of the formation of 2-methylpropane, just as that of *n*-pentane and 2-methylbutane, diminished drastically with increasing hydrogen pressure (Fig. 5). This is exactly what one observes for one of the rearrangement reactions over Pt and Pd, namely for dehydro-isomerization of isohexanes to aromatics which presumably involves a carbene-type skeletal rearrangement pathway (*13, 28*). Previous studies (*7–9, 22*) and the results in Fig. 5 corroborate that the chain lengthening is strongly suppressed by a large excess of hydrogen which in turn decreases the selectivity of the carbene route of isomerization.

Since the presence of H_2 influences the dissociation of C–H bonds the partial pressure of H_2 should play an important role in governing the mechanism of isomerization. At low ratios of H_2/HC a carbene–olefin mechanism seems to be the prevailing route of isomerization over Pd, Ni, and Ni–Ag catalysts. Large excess of H_2 should promote skeletal rearrangement via Rooney–Samman mechanism as this mechanism requires formation of a monoadsorbed intermediate (*10*).

(iii) The experiments with Ag-rich samples, 85 and 89 at.% Ag, respectively, might provide further evidence for an external C_1 migration. At these compositions, owing to the hindrance of the C–C bond rupture, the selectivity of isomerization of *n*-butane decreased whereas the selectivity of 2-methylbutane formation is only slightly affected (Fig. 3). It is of interest that the selectivity of *n*-pentane formation is still rising at these Ag concentrations. This phenomenon can be interpreted by the extensive steric crowding of the Ni sites which allows only terminal insertion of CH_2. In fact the carbon coverage of the working catalyst sur-

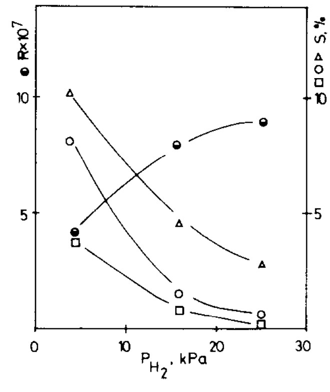


FIG. 5. The rate of *n*-butane consumption (●) in mol s^{-1} g_{met}^{-1} and the selectivity of 2-methylpropane (△), 2-methylbutane (○), *n*-pentane (□) formed from *n*-butane (p_{HC} = 4 kPa, T = 553 K) on a 65 at.% Ag–Ni sample.

TABLE 4

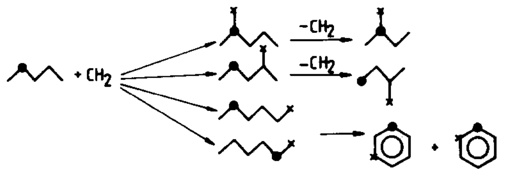
The Relative Specific Activity of Benzene (ρ_B/ρ^0_{nP}), 2-Methylpentane (ρ_{2MP}/ρ^0_{nP}), and 2-Methylbutane (ρ_{2MBut}/ρ^0_{nP}) in Transformation of 2-[C^{14}]-*n*-Pentane

Catalyst 5 wt% metal/SiO_2	p_{HC} (kPa)	p_{HC}/p_{H_2}	T (K)	ρ_B/ρ^0_{nP}	ρ_{2MP}/ρ^0_{nP}	ρ_{2MBut}/ρ^0_{nP}
0 at.% Ag–Ni	4	0.73	563[a]	1.17 ± 0.02	1.12 ± 0.05	1.11 ± 0.05
	4	0.88	554	1.13 ± 0.02	1.13 ± 0.06	1.17 ± 0.05
35 at.% Ag–Ni	4	0.88	553	1.18 ± 0.01	1.17 ± 0.03	1.15 ± 0.03
85 at.% Ag–Ni	4	0.88	553[a]	1.16 ± 0.05	1.17 ± 0.04	1.10 ± 0.06

[a] Average of 3 measurements, otherwise average of 5.

face, expressed in mg C g_{Ni}^{-1} (Fig. 4), is the highest with the Ag-rich sample. The hydrogenation experiments with chemisorbed *n*-hexane (the value of RH% is given in Fig. 4) are in accordance with this observation since the hydrogenation desorption activity of the Ag–Ni samples is the lowest at 85 at.% Ag.

(iv) The experiments with 2-[^{14}C]-*n*-pentane over Ni/SiO_2 and 35 at.% Ag–Ni catalysts do substantiate the carbene addition–methyl abstraction mechanism. The relative specific activity of benzene (ρ_B/ρ^0_{nP}), 2-methylpentane (ρ_{2MP}/ρ^0_{nP}), and 2-methylbutane (ρ_{2MBut}/ρ^0_{nP}) are summarized in Table 4. The specific activity of benzene and that of 2-methylpentane and 2-methylbutane (expressed as counts/mol HC) exceeds that of 2-[^{14}C]-*n*-pentane. The relative specific activities are observed to vary between 1.10 and 1.18, suggesting that the specific activity of the CH_2 units is about one-fifth of the specific activity of *n*-pentane. (This result seems to indicate that because of the "zip-fastener-like" fragmentation there is a very rapid mixing of the CH_2 units. Other results (*29*) show that this is the situation even over Pt-black.) The reaction route in Scheme 2 explains why the specific activity of 2-methylbutane should be higher than that of *n*-pentane in the case of the carbene addition–methyl abstraction mechanism.



SCHEME 2. Transformation of 2-[^{14}C]-*n*-pentane.

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