Isomerization of Heptanes over a Palladium-Zeolite Catalyst

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The isomerization of heptane isomers, heptane, 2- and 3-methylhexane, 3-ethylpentane, and 2,3- and 2,4-dimethylpentane, was investigated kinetically over a palladium-zeolite catalyst in the presence of hydrogen at 280—350 °C. First-order rate constants of 11 reaction paths were given with their activation energies and pre-exponential factors. The reaction scheme network including 22 isomerization steps among 9 isomers was constructed through the detailed analysis of primary and secondary reaction products from the individual isomers. Finally, the several proposed isomerization mechanisms were examined on the basis of the present experimental results.

The skeletal isomerization of paraffinic hydrocarbons has been extensively studied over the so-called dual functional catalysts.[1-4] The mechanism has been explained as follows: dehydrogenation of paraffins and hydrogenation of isomerized olefins take place on the metallic site and the formation of carbonium ions from olefins and their rearrangements do on the acidic site. However, the isomerization of butane was discovered by Anderson and Avery[5] to occur on the evaporated film of platinum metal. Boudart and Ptak[6] have reported the isomerization of neopentane to occur on the metal surface of platinum, iridium and gold supported on alumina. Corolleur *et al.*[7] have insisted that the isomerization of hexanes takes place exclusively on the metal site of platinum-alumina, although the intermediate postulated by them differs from that by Anderson and Avery.[5] On the structure of the intermediate, it was proposed recently by Lanewala *et al.*[8,9] that hexane isomerized *via* adsorbed dimeric intermediate on a palladium-zeolite catalyst.

Only a few reports,[10,11] however, have been reported on the isomerization mechanism of heptane isomers. Numbers of isomers may make the system complicated, but the informations therefrom will be plenty. The first aim of the present study is to clarify the detailed reaction paths of heptane isomerization on the palladium-zeolite catalyst through the detailed analysis of the products as well as the kinetic examinations of their formations. The second aim is to select the reasonable mechanism among the several proposed mechanisms on the basis that it should not conflict with the obtained results in the present study.

Experimental

Commercially available *n*-heptane (HP; 99.9 mol%), 2-methylhexane (2MHX; 99.4), 3-ethylpentane (3EP; 99.2), 2,4-dimethylpentane (24DMP; 99.4), 2,3-dimethylpentane (23DMP; 94.7), and 3-methylhexane (3MHX; 96.5) were used without further purifications. Palladium-zeolite catalyst was prepared from Pd(II) tetraammine chloride and Na-13Y zeolite in the aquatic solution by an ion exchange technique.[12] The amount of palladium metal was 3.0 wt%. The Cl ion free dried catalyst sieved 10 to 20 mesh was calcined in the air at 400 °C for 4 hr, followed by the reduction in the dried and deoxygenated hydrogen stream at 500 °C for 6 hr. Thus the composition of the catalyst is expected to be mostly a metallic palladium on H-Y zeolite, although the X-ray diffraction pattern for metallic palladium was not so clearly obtained.

Experiments were conducted by use of two different reaction apparatus. The one was an usual continuous flow-type apparatus. The reactor was made of a pyrex glass tube (18 mm i.d.) furnished with a co-axial thermowell (8 mm o.d.), in which 2.5 g (apparent volume, 5 ml) of the unreduced catalyst was packed. After the reduction of the catalyst, the temperature was settled to begin the isomerization reaction by passing the hydrogen stream through a reactant container which was dipped in an ice-water bath. The concentration of the reactant was maintained at 1.0 mol%. Variations on the concentration were attained by controlling the streaming ratio of hydrogen through the reactant container. The hydrogen pressure was maintained at 770 mmHg. The space velocities* were between 0.2 and 5.0 s^{-1}. The reaction products were analyzed by glc equipped with a flame ionization detector and a capillary column coated with squalane.

The other apparatus was of a conventional micro pulse reactor which was linked directly to a glc equipped with a thermal conductivity detector and a packed column containing dioctylphthalate on celite-545. A small amount (0.25 g) of the unreduced catalyst was placed at the bottom of a U-shaped pyrex tube of 5 mm i.d., then it was reduced. Hydrogen pressure was maintained at 1400 mmHg. Mostly 2.0 μl of the reactant were injected in each run by a microsyringe into the preheated hydrogen stream.

Results

Isomerization of HP and 3MHX with the Continuous Flow-type Apparatus. The experimental results were listed in Table 1. The isomerization of HP was effectively catalyzed on the palladium-zeolite catalyst above 280 °C. The predominant products were 2MHX and 3MHX. The hydrogenolysis products were very small in their amounts. The selectivity for isomerization was found to exceed 97% even at the most severe condition. Among minor isomerized products, 3EP and 23DMP were formed in distinct amounts from the early stage of the reaction.

In the case of 3MHX feed, the predominant products were 2MHX, 3EP, 23DMP, and HP.

Table 2 shows the resulted conversions in the case of HP isomerization at 305 °C by varying the reactant concentration between 0.6 and 2.0 mol%. The invariance of conversion confirms the first-order rate

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* The space velocity was defined as the ratio of the volumetric rate of inlet gas at the reaction temperature and pressure to the apparent packed volume of unreduced catalyst. The reciprocal of which was defined as the contact time.

Table 1. Experimental results with the continuous flow-type apparatus

Reactant	Temp. (°C)	1/SV (s)	Obtained hydrocarbons (mol%)										
			C_1-C_3	C_4-C_6	22DMP	24DMP	33DMP	2MHX	23DMP	3MHX	3EP	HP	Others[b]
HP	280	0.66	—	0.04	—	—	—	0.57	0.05	0.78	0.15	98.36	—
		1.31	—	0.04	—	—	—	1.24	0.13	1.62	0.30	96.67	—
		2.62	—	0.04	0.04	—	—	1.96	0.12	2.59	0.19	95.10	—
		5.24	—	0.01	0.14	0.09	0.02	4.04	0.27	4.84	0.41	90.18	—
		10.5	0.04	0.13	0.47	0.41	0.28	7.87	0.71	8.37	0.64	81.08	—
	300	0.32	—	0.04	0.01	—	—	0.86	0.14	1.19	0.06	97.70	—
		0.63	0.01	0.06	0.02	—	—	1.57	0.09	2.20	0.27	95.78	—
		1.27	0.05	0.06	0.02	—	—	2.86	0.18	3.61	0.28	92.94	—
		2.53	0.08	0.13	0.21	0.16	0.11	5.69	0.46	6.91	0.57	85.68	—
	320	0.20	—	0.03	0.03	0.03	—	1.94	0.14	2.52	0.20	94.97	0.14
		0.30	—	0.06	0.08	0.06	—	2.75	0.21	3.52	0.27	92.97	0.08
		0.59	0.08	0.12	0.21	0.20	0.13	5.82	0.52	6.94	0.58	85.26	0.14
		1.18	0.20	0.19	0.48	0.48	0.34	9.16	0.96	10.77	0.86	75.41	1.15
		2.36	0.67	0.70	1.51	1.40	0.96	15.36	2.47	17.57	1.40	57.65	0.31
	340	0.10	0.10	0.04	0.06	0.08	0.08	2.01	0.20	2.48	0.21	94.65	0.09
		0.20	0.14	0.06	0.16	0.17	0.13	3.78	0.45	4.66	0.38	89.98	0.09
		0.30	0.24	0.13	0.26	0.24	0.18	5.46	0.60	6.35	0.46	86.00	0.08
		0.59	0.29	0.35	0.63	0.65	0.46	10.44	1.45	12.00	0.95	72.48	0.30
		1.18	0.91	1.06	1.81	1.85	1.35	10.14	1.74	11.34	1.83	67.39	0.60
3MHX	290	0.32	0.01	0.01	0.16	0.14	0.12	6.54	0.74	85.92	3.51	0.61	2.22
		0.64	0.02	0.02	0.37	0.31	0.20	11.68	1.37	79.17	3.64	1.18	2.09
		1.29	0.06	0.09	0.71	0.64	0.46	18.41	2.20	68.75	4.11	2.40	2.21
		2.57	0.15	0.19	1.31	1.14	0.81	23.75	3.14	58.49	4.28	4.53	2.29
—[a]		—	—	—	—	—	—	0.18	—	96.50	0.84	—	2.48

a) Feed 3MHX. Unidentified impurities (2.48 mol%) are refractory to the reaction. b) Unidentified substances, presumably cycloalkanes.

Table 2. Effect of concentration of HP upon conversion at 305 °C, 1/SV=2.5 s

Concentration of HP (mol%)	Conversion (%)
0.6	21.3
1.2	21.7
2.0	22.1

equation in respect to HP under the condition of excess hydrogen. Moreover, the first-order rate plots were confirmed to hold for HP isomerization at 280, 300, 320 and 340 °C, and also for 3MHX isomerization at 290 °C, by use of the data in Table 1.

Isomerization of Six Heptane Isomers with the Micro Pulse Apparatus. HP, 3MHX, 2MHX, 3EP, 24-DMP, and 23DMP were subjected to isomerization by use of the micro pulse apparatus. Injection of 2.0 μl of reactants in a hydrogen stream resulted in a constant contact time of 0.2 s. The first-order rate equation was confirmed for all reactants by varying the injection amount and obtaining the same conversions and product distributions. The intrinsic deviations existed for the rate constants of HP and 3M-HX isomerizations between the results of the two different apparatus. i.e., average 40.0% lower by the micro pulse reactor than by the continuous flow type one. As the reactant to H_2 molar ratio was sufficiently low, the small deviations could be attributed to the difference of temperature distribution through the catalyst layer. So that the coefficient, 1.40, was introduced for the interconversion between the results obtained with the two apparatus.

The experiments were performed in the range of temperature where the conversions resulted between 2 and 30% of reactant isomers. The followings are the reactants, the temperature necessary to achieve the conversion of 10%, obtained products and their percentages in the total products.

HP	346 °C	3MHX(43.5%), 2MHX(34.2%), 23DMP(4.3%), 3EP(3.7%), 24DMP(1.6%), 22DMP(1.5%)
3MHX	308 °C	2MHX(59.0%), 3EP(30.6%), HP(6.2%), 24DMP(1.0%), 22DMP(1.0%), 33DMP(0.7%)
2MHX	312 °C	3MHX(86.1%), 3EP(4.0%), HP(3.9%), 24DMP(2.3%), 22DMP(2.1%), 33DMP(1.2%)
3EP	277 °C	3MHX(96.5%), 2MHX(2.7%)
24DMP	305 °C	23DMP(74.0%), 33DMP(10.9%), 3MHX(5.3%), 2,2,3-trimethylbutane(3.7%), 3EP(1.9%), 2MHX(1.0%)
23DMP	269 °C	24DMP+22DMP(64.7%), 33DMP(29.0%), 2MHX(5.9%)

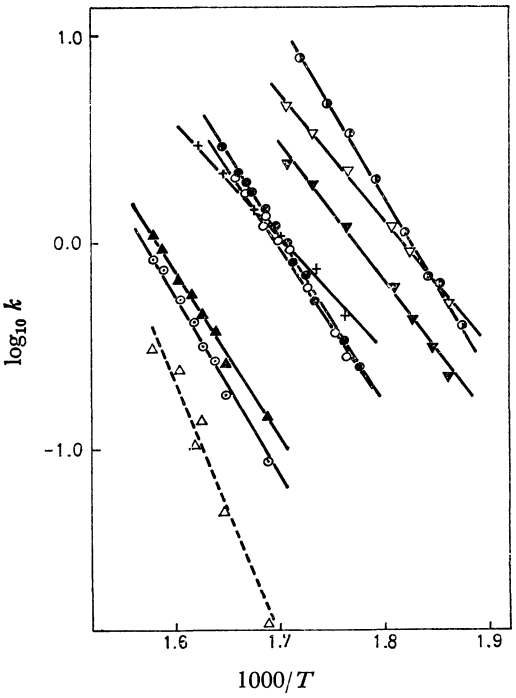

Fig. 1. Arrhenius plots of isomerization of heptane isomers.
⊙, HP → 2MHX; ▲, HP → 3MHX; ●, 2MHX → 3MHX; ○, 3MHX → 2MHX; ◑, 3EP → 3MHX; +, 24DMP → 23DMP; ▼, 23DMP → 33DMP; ▽, 23DMP → 24DMP+22DMP; △, HP → *n*-Hexane.

Arrhenius plots of the 9 main primary reactions including hydrogenolysis of HP were shown in Fig. 1. Activation energies and pre-exponential factors of the reactions above were tabulated in Table 3 along with the rate constants normalized at 320 °C. Obtained data for the two relatively minor reactions, 3MHX→HP and 2MHX→HP, were also tabulated.

Discussion

The Reaction Scheme. Based on the primary product distributions obtained in the preceding section, the net-work of the reaction path was constructed as shown in Fig. 2. This reaction scheme is composed of 22 isomerization steps among 9 isomers of heptane, neglecting hydrocracking reactions. The characteristic features of the present scheme are that 3EP is generated exclusively from 3MHX and that 23DMP mediates between methylhexanes and other dimethylpentanes. The first proposal is based on the fact that the primary product of 3EP isomerization was solely 3MHX, and that 30.6% of product was 3EP in the reverse reaction of 3MHX. The second proposal is based on the fact that 23DMP is generated prior to other dimethylpentanes in the isomerization of HP and of 3MHX as is seen in Table 1. Besides, the reaction of 23DMP proceeded rapidly to 24DMP, 22DMP, and 33DMP. Although 24DMP and 22DMP were not separated as two distinct gas chromatographic peaks in this case, the amount of them could duly be estimated as one to one from the peak. In the reactions of HP, 3MHX, and 2MHX, the production ratio of 24- to 22-DMP were almost one to one. In this connection, however, the minor but direct reaction path from 2MHX to 24DMP should exist, because the molar production ratio of 24DMP to 33DMP in the reaction of 2MHX is larger (*ca.* 2.0) than that in the reaction of 3MHX (*ca.* 1.4).

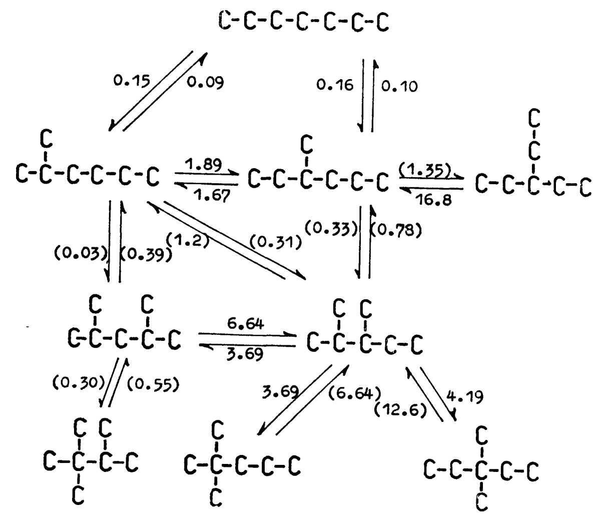

Fig. 2. The proposed isomerization scheme of heptane isomers. Rate constants obtained and (evaluated) at 320 °C.

The values of rate constants normalized at 320 °C were prepsented in Figure 2. Those values with parentheses mean the poor reliability of data because of the very small amounts of reaction products and the lack of reverse reactions in the present experiments. They were evaluated not to conflict with the experimental results and the reported equilibrium distribution among 9 isomers.[13] By use of the above values, the numerical integrations of the first-order rate equations were performed by the RUNGE-KUTTA method to examine the validity of the postulated reaction scheme. The results of calculation for the isomerization of HP at 280, 300, 320, and 340 °C, and of 3MHX at 290 °C agreed satisfactorily with the experimental plots of Table 1. Figures 3(a), (b), and (c) show the product distribution *vs.* conversion curves calculated for the reaction of HP at 320 °C together with the experimental results. Figures 4(a) and (b) show the result of examination for the reaction of 3MHX at 290 °C. In this case, product yield *vs.* reciplocal SV curves were adopted.

Examination of Several Proposed Reaction Mechanisms. There have been proposed several mechanisms for the skeletal isomerization of alkanes over acidic and metallic catalysts. Isomerization on the acidic catalysts has been postulated to occur as the carbonium ion mechanism through the 1,2-shift of alkyl anion.[14] Recently, through the examination of the reaction in superacid, the nonclassical protonated cyclopropane was proposed to be an intermediate.[15]

Corolleur *et al.*,[7] and Barron *et al.*[16] adopted the cyclopentane type intermediate on the metal surface. The former used isotope-labeled hexanes on the platinum–alumina catalyst. Anderson and Avery[5] proposed an entity of the 1,3-triadsorbed intermediate by which the skeletal rearrangement was accomplished

Table 3. Kinetic data for the isomerization of heptanes

Reaction	Temperature range (°C)	Activation energy (kcal/mol)	log A	k at 320 °C (V/V/s)
HP → 3MHX	320—360	38.3	13.3	0.158
HP → 2MHX	320—360	41.3	14.2	0.153
3MHX → HP	290—340	32.3	11.1	0.101
3MHX → 2MHX	290—340	36.5	13.7	1.67
2MHX → HP	290—340	33.9	11.5	0.092
2MHX → 3MHX	290—340	37.7	14.2	1.89
3EP → 3MHX	250—310	38.0	15.2	16.8
24DMP → 23DMP	270—330	33.1	13.0	6.64
23DMP → 24DMP+22DMP	260—320	28.2	11.3	7.38
23DMP → 33DMP	260—320	30.9	12.0	4.19
HP → *n*-hexane	320—380	49.0	16.0	0.0093

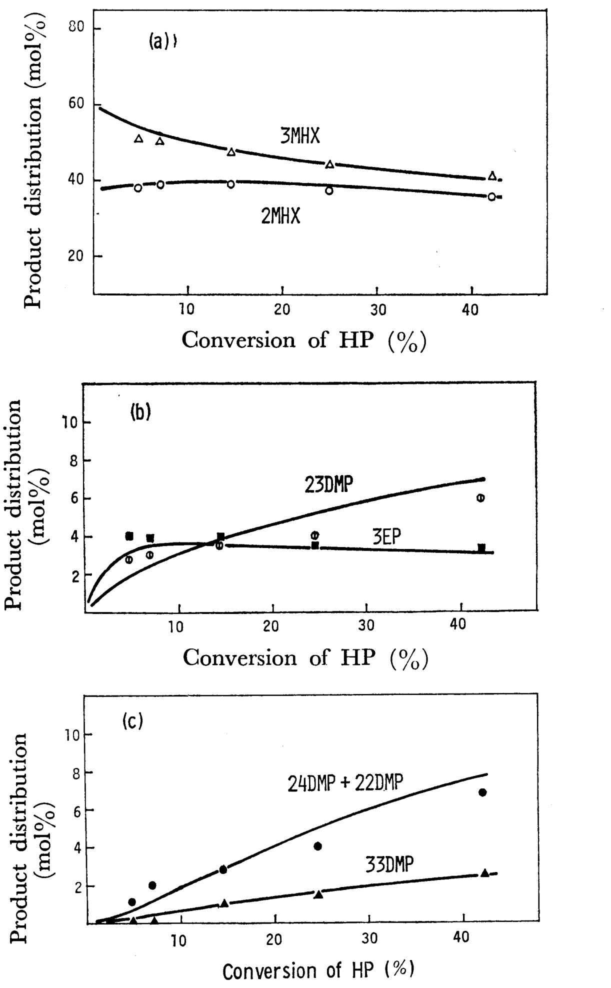

Fig. 3. Calculated (solid lines) and obtained (points) product distribution in the isomerization of HP at 320 °C.

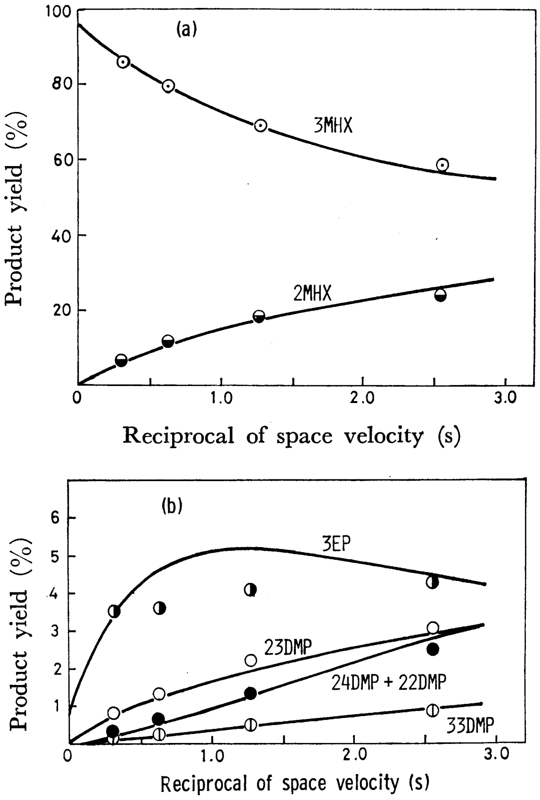

Fig. 4. Calculated (solid lines) and obtained (points) product yield in the isomerization of 3MHX at 290 °C.

via a bridged transition state. The intermediate was considered to be stabilized by transferring a fractional electron from the adsorbed hydrocarbon to the surface metal. This mechanism was supported by themselves through a calculation of the Hückel molecular orbitals.[17] Boudart and Ptak[6] discovered that platinum, iridium and gold, excluding palladium, catalyzed isomerization of neopentane and proposed that metals of sufficient electro-negativity were capable to catalyze the reaction. The intermediate, postulated by them, is a 1,3-triadsorbed species which has some character of the carbonium ion.

Lanewala *et al.*[8,9] conducted the isomerization of hexanes on a palladium–zeolite catalyst. They have proposed a bimolecular mechanism on the surface metal on the basis of their detailed product analyses.

There exists some ambiguity for the supported metal catalysts whether their active sites are metallic or acidic. In the present discussion, the several mechanisms described above will be examined from the point of proposed intermediates referring to the obtained reaction paths in Fig. 2. Three reaction steps are worth while to consult in the evaluation of the above mechanisms, *i.e.*, (i) simultaneous formations of 2MHX and 3MHX from HP, (ii) reversible isomerization between 3EP and 3MHX, and (iii) reversible reaction between 23DMP and 24DMP.

Formally, the present results are well explained by the carbonium ion mechanism for acidic catalysts if the methyl and ethyl groups shift to the adjacent carbon atom in the reactions (i) and (iii), and in the reaction (ii), respectively. But this mechanism is criticized not to occur on a metal surface.5)

It seems reasonable that reaction (ii) proceeds *via* the cyclopentane type intermediate.7,16) However, the reaction (i) and (iii) could not be interpreted by the same intermediate. They require participations of six- and four-membered cyclic intermediates, respectively. The proposal by Lanewala *et al.*8,9) does not hold in the present results because no trace of octane isomers was detected and no evidence of direct formation of 23DMP from HP was found.

The remaining two mechanisms, those involve 1,3-triadosorbed intermediate5,6) and the protonated cyclopropane,15) cannot be distinguished by the present results, because both mechanisms lead to the same conclusion in regard to the cleavage and the formation of C–C bonds. All the reactions in the scheme are interpreted in terms of either of these mechanisms.

Activation energies obtained in the present work for the reactions of six heptane isomers were 30—40 kcal/mol. These values are larger than those found on the acidic catalysts (15—25 kcal/mol)18–20) and smaller than those on the metallic catalysts (40—50 kcal/mol).21) Namely, the palladium–zeolite catalyst in the present work exhibits a metallic character in regard to the activation energy and, at the same time, an acidic character in regard to its activity for the isomerization, because the pure palladium metal has been reported not to catalyze the isomerization of hydrocarbons.6)

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