JOURNAL OF CATALYSIS **105**, 65–70 (1987)

On the Mechanism of Aromatization of 3-Methylpentane over Ni Catalysts

A. SÁRKÁNY

Institute of Isotopes of the Hungarian Academy of Sciences, P.O. Box 77, H-1525 Budapest, Hungary

Received June 30, 1986; revised November 3, 1986

The mechanisms of aromatization of C_6 and C_7 alkanes have been investigated over Ni catalysts. On the basis of radioactive measurements with [3-^{14}C]methylpentane it was concluded that benzene is formed both by a CH_x addition–abstraction mechanism and by intramolecular rearrangements. A change of the product selectivity with hydrogen pressure has been interpreted in terms of a change in the ensemble size of Ni governed by strongly adsorbed hydrocarbon fragments. © 1987 Academic Press, Inc.

INTRODUCTION

Metal-catalyzed aromatization of methylpentanes is generally accepted to require both C_5-cyclization and bond-shift activity (*1–3*). Over Ni and Co catalysts aromatization was observed (*4–6*) to be accompanied by chain lengthening homologation, and the aromatization selectivity could be correlated with the ability of methylpentanes to participate in CH_x addition. It was concluded that on Ni and Co under those particular conditions CH_x addition to the terminal carbon atoms of a C_5 chain followed by 1,6-dehydrocyclization contributed to aromatization. The low specific radioactivity of toluene (*6*) formed from mixtures of 2-methylpentane and [^{14}C]benzene under conditions when [^{14}C]benzene was not fragmented enabled a direct benzene alkylation route to be rejected.

The participation of C_5 cyclization–bond-shift rearrangement in the formation of aromatics seems to remain hidden as the C_5 cyclization activity of Ni is not unambiguously demonstrated. In a comprehensive study (*7*) no C_5 cyclization activity of Ni powder was observed in the transformation of 3-methylpentane. On the other hand, formation of methylcyclopentane and methylpentanes was established with Ni black (*8*) and the increase of dispersion enhanced the selectivity of formation of these products over Ni films (*9, 10*). With catalysts containing 1- and 6-nm Ni crystallites the selectivity for dehydrocyclization at 622 K was observed to be only 3 and 1%, respectively, in transformation of *n*-hexane (H_2/HC = 16) (*11*).

The work presented here aimed to investigate the aromatization of methylpentane on a group of Ni catalysts. In particular, attempts have been made to separate the CH_x addition–abstraction route of aromatization from the intramolecular routes (C_5 cyclization–ring expansion (*2a*) and vinyl shift (*2b*) plus 1,6-dehydrocyclization) by measuring the specific radioactivity of benzene formed from [3-^{14}C]methylpentane. The effect of hydrogen pressure on product distribution is discussed in terms of the continuously varying size of Ni ensembles caused by changes in the amounts of carbonaceous deposits.

EXPERIMENTAL

The static circulation system (0.185 dm^3) used was the same as in the previous studies (e.g., Ref. (*12*)). The hydrocarbons were separated at 60°C with a 6-m-long column filled with 16 wt% squalane or with a 50-m-long capillary column wetted with squalane. In the radiotracer studies the carrier gas was split after the column. A part,

0021-9517/87 $3.00

TABLE 1

Product Selectivity (%) over Ni Catalysts

Catalyst	Hydrocarbon	Temperature (K)	α (%)	$<C_n$	B	T	Others (%)
63-Ni-Dep	*n*-P	630	4.7	85.5	8.2	5.2	1.1 2MP
63-Ni-Dep	CP	580	3.3	91.7	6.7	1.6	7.7 MCP
63-Ni-Dep	CP	637	8.3	70.2	19.6	10.2	0.3 MCP
63-Ni-Dep	3MP	637	10.2	68.9	18.9	12.2	0.2 EBz; 0.8 (m + p)X; 0.3 oX
59-Ni-Imp	3MP	623	6.6	72.1	17.6	10.3	0.4 EBz; 1.6 (m + p)X; 0.2 oX
59-Ni-Imp	3MH	631	12.2	49.3	33.6	17.2	0.2 EBz; 2.4 (m + p)X; 0.3 oX
63-Ni-Dep	2,4-DMP	623	12.3	94.1	4.2	1.7	—
63-Ni-Dep	2,3-DMP	623	10.6	91.4	6.3	2.3	—
16-Ni-Imp	3MP	633	10.3	84.4	6.7	8.9	—
16-Ni-Imp	2,4-DMP	643	7.8	99.45	0.43	0.12	—

Note. α, conversion; $<C_n$, fragments; B, benzene, T, toluene; n-P, *n*-pentane; CP, cyclopentane; MCP-methylcyclopentane; 3MP, 3-methylpentane; 3MH, 3-methylhexane; 2,4-DMP, 2,4-dimethylpentane; 2,3-DMP, 2,3-dimethylpentane; EBz, ethylbenzene; oX, mX, and pX, *ortho, meta,* and *para*-xylene, respectively. Conditions: 0.08–0.15 g catalyst; P_{HC} = 2.66 kPa; $H_2/HC \simeq 2$.

about $\frac{1}{10}$, went to the FID and about $\frac{9}{10}$ was passed through a proportional counter. Hydrocarbons before entering the proportional counter were burned to CO_2 over CuO at 600°C. CO_2 formed was dried over P_2O_5.

Catalysts designated Ni-B, 13-Ni-Imp, 63-Ni-Dep, and 59-Ni-Imp were used in this study. The initial number is the percentage dispersion measured by hydrogen chemisorption, and B, Imp, and Dep, respectively, indicate metal black, impregnation using the method of incipient wetness, and precipitation of $Ni(NO_3)_2$ by urea onto the surface of SiO_2 aerogel. The preparation and characterization of the samples are presented in previous papers (*5, 13, 14*).

RESULTS AND DISCUSSION

The selectivity of products measured at a H_2/hydrocarbon composition of 2 : 1 (2.66 kPa hydrocarbon) and the effect of hydrogen pressure on the formation of products from 3-methylpentane over 59-Ni-Imp are presented in Table 1 and Fig. 1, respectively. The results with [3-^{14}C]methylpentane are collected in Table 2. The specific radioactivity of benzene and toluene is divided by the specific radioactivity of 3-methylpentane.

Under the hydrogen-deficient conditions investigated fragmentation is the main reaction route. However, aromatization associated with CH_x addition is clearly observable as is indicated by the formation of benzene from *n*-pentane and cyclopentane and that

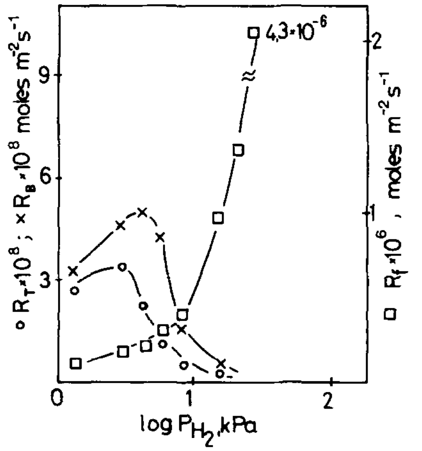


FIG. 1. Rate of formation of benzene (×) and toluene (O), and rate of fragmentation (□) from 3-methylpentane as a function of hydrogen pressure on 59-Ni-Imp at 633 K. Conditions: 0.12 g catalyst; P_{HC} = 2.66 kPa.

TABLE 2

Transformation of [3-^{14}C]Methylpentane on Ni and Pt Catalysts

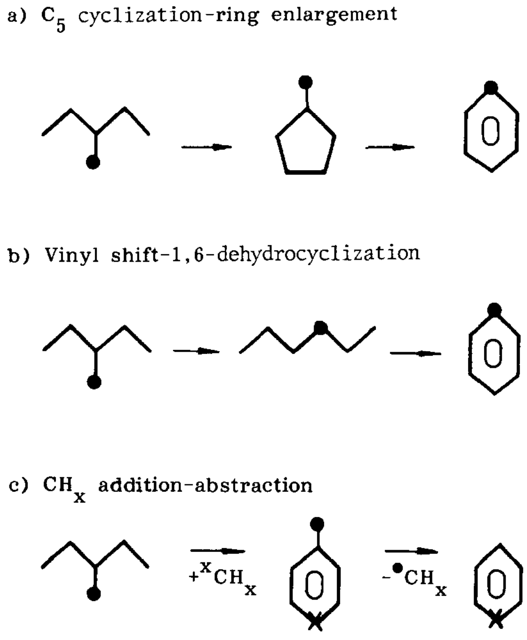
Catalyst	Temperature (K)	H_2/HC	α (%)	ρ_B/ρ_{3MP}	ρ_T/ρ_{3MP}	ω^{CH_x} (%)	ω^I (%)	B (%)
Ni-B	623	1.78	3.7	0.89	1.08	11.9	88.1	5.7
Ni-B	623	1.78	13.2	0.92	1.05	8.4	91.6	10.2
Ni-B	641	2.26	8.9	0.88	1.12	13.6	86.4	4.7
16-Ni-Imp	631	1.55	7.1	0.83 ± 0.05	1.17 ± 0.06	20.4	79.6	7.2
16-Ni-Imp	631	0.66	17.3	0.87	1.11	14.6	85.4	9.8
63-Ni-Dep	633	1.43	12.6	0.83	1.10	18.8	81.2	10.2
63-Ni-Dep	633	2.43	8.6	0.85	1.07	16.1	83.9	12.1
59-Ni-Imp	637	1.66	17.9	0.81	1.19	23.4	76.6	18.9
81-Pt-Imp	603	2.13	9.9	0.98 ± 0.06	1.05	2.1	97.9	38.1
81-Pt-Imp	726	1.12	10.3	0.95	1.08	5.4	94.6	64.1
81-Pt-Imp	726	2.13	21.2	0.87	1.06	13.8	86.2	69.3

Note. α, conversion; ρ_B, ρ_T, and ρ_{3MP}, specific radioactivity of benzene, toluene, and 3-methylpentane, respectively; ω^{CH_x} and ω^I, contribution to benzene formation (%) by CH_x addition–abstraction and by intramolecular routes (ω^{CH_x} (%) $= 100 * (\rho_{3MP} - \rho_B)/(2\rho_{3MP} - \rho_T)$; $\omega^I = 100 - \omega^{CH_x}$); B, selectivity of benzene formation. Conditions 0.083–0.2 g catalyst; P_{HC}, 2.66 kPa.

of toluene from 3-methylpentane. From 3-methylhexane the selectivity of formation of benzene and toluene is commensurable, suggesting that the loss of a CH_x group is rapid in the chemisorption phase. While the CH_x addition–abstraction mechanism is discernible the contribution of the intramolecular routes to benzene formation is less clear. With increasing dispersion the selectivity of aromatization increases, which might point, for example, to an increased probability of C_5 cyclization on low coordination sites (*9, 10*) or to a less severe poisoning of CH_x-forming sites (*4, 11*). The hydrogen sensitivity of the transformation of 3-methylpentane in Fig. 1 does not provide sufficient information for the C_5 cyclization route. With increase of the partial pressure of hydrogen the formation of toluene decreases and the formation of benzene passes through a maximum. In principle, the increasing yield of benzene might stem from the hydrogenolysis of chain-lengthening products or from the enhanced probability of C_5 cyclization–ring enlargement.

Inspection of the radioactivity results obtained using [3-^{14}C]methylpentane as reported in Table 2 brings the possibility to determine the contribution of the CH_x addition–abstraction route to the benzene formation. First, we consider the specific radioactivity of toluene. The specific radioactivity of this product is 5–19% higher than that of the starting [3-^{14}C]methylpentane, suggesting that the probability that a CH_x unit added contains radioactive carbon is 0.05–0.19. The results on Ni catalysts are somewhat at variance with the observation over Pt black (*15*). On the latter metal due to the hindrance of the rupture of the primary–tertiary C–C bond the CH_x unit did not contain radioactive carbon. If in 3-methylpentane each carbon atom were equivalent with respect to CH_x formation, then the specific radioactivity of CH_x should be $\frac{1}{6} = 0.17$. On the average the observed values in Table 2 are not very far from this value.

Whereas the specific radioactivity of toluene is higher the specific radioactivity of benzene is less than that of 3-methylpentane over Ni samples. The specific radioactivity of benzene should remain identical with that of 3-methylpentane if the aromatization takes place selectively via the C_5 cyclization–ring expansion mechanism



SCHEME 1. Routes of benzene formation from [3-^{14}C]methylpentane.

(Scheme 1). The same holds in respect of the vinyl shift (*2b*) plus 1,6 dehydrocyclization route. The CH_x addition–abstraction route, on the other hand, alters the specific radioactivity of benzene since the hydrogenolysis of the methyl group in toluene results in the loss of radioactivity label. Consequently, the specific radioactivity of benzene is less than that of 3-methylpentane (Scheme 1).

The contribution of the CH_x route to benzene formation was calculated taking into account the specific radioactivity of toluene and benzene formed: these results are collected in column 7 of Table 2. The selectivity of the sum of the intramolecular routes is presented in the penultimate column. Here one might assume considering the results with Ni–Cu alloys (*8*) that on highly dispersed Ni the rearrangement takes place essentially by the cyclic mechanism, i.e., route **a** in Scheme 1 is largely predominant. The vinyl shift plus 1,6-dehydrocyclization route is likely to contribute to some extent to benzene formation on Ni-B and 16-Ni-Imp. According to the data available on the selectivity of hexane formation from 3-methylpentane, the percentage of cyclic mechanism decreases from 95 to 55% as the H/Pt ratio decreases from 1 to 0.05 (*16*).

Inspection of the results in Table 2 shows that with each Ni catalyst investigated the intramolecular way of benzene formation is preferred to the CH_x addition–abstraction route although the increase of the H_2/HC ratio and the temperature seem to favor to some extent the CH_x route. Over the highly dispersed sample more benzene is formed by the CH_x route. This result might be explained by the less severe poisoning of the hydrogenolysis activity of small Ni crystallites (*5, 11*). For the sake of comparison, experiments with 3 wt% Pt/SiO_2 of 79% dispersion are included in Table 2 (last three rows). At 603 K the specific radioactivity of benzene (measured together with methylcyclopentane) agrees with 3-methylpentane, within experimental error, which in turn confirms that aromatization takes place exclusively via intramolecular rearrangements. Only in experiments at 726 K, shown in the last two rows in Table 2, does the specific radioactivity of benzene deviate from that of 3-methylpentane, by 5 and 13%, respectively.

The mechanism of the intramolecular routes on Ni requires some discussion. It is an interesting feature of the transformation of 3-methylpentane that although the radioactive measurements provide evidence for reaction routes **a** and **b** in Scheme 1 still the saturated products of C_5 cyclization and isomerization are absent in the gas phase. Increases of the partial pressure of hydrogen did not facilitate the formation of the saturated products of C_5 cyclization or of the vinyl shift; only the rate of fragmentation accelerated, as is shown in Fig. 1.

The peculiarity of aromatization over Ni catalysts might be explained if one considers the surface state of the working catalyst. The change of the product distribution pattern as a function of partial pressure of hydrogen can be interpreted as a consequence of an ensemble effect (*8, 17–19*) caused by trapped hydrocarbons (carbonaceous deposits). The decrease of the partial pressure of hydrogen enhances the formation of "deeply" dissociated hydrocarbon species which under the given experimental conditions (H_2/HC ratio, temperature, etc.) remain trapped on the surface. The presence of these deposits which are formed at the very early stage of the hydrocarbon transformation (*5, 20*) affects the size of the working Ni ensembles. The lower the partial pressure of hydrogen the larger is the "carbon" coverage on the surface. In consequence, the probability of finding large Ni ensembles which catalyze deep fragmentation decreases (*8, 18, 19*). As shown in Fig. 1, the hydrogenolysis activity dropped by about a factor of 45 when the partial pressure of hydrogen decreased from 26.6 to 5.32 kPa. The partial poisoning of the surface, i.e., the formation of small ensembles, promotes C_5 cyclization (*8, 18*) but this reaction step is immediately followed by ring expansion and dehydrogenation to aromatics because of the low virtual pressure of hydrogen on the surface. Aromatization by vinyl shift might also be expedited in a low excess of hydrogen. The increase of the H_2/HC ratio should facilitate the desorption of alkanes formed by C_5 cyclization or vinyl shift but with increasing partial pressure of hydrogen the size of the working Ni ensembles, and hence the probability of finding contiguous, unperturbed Ni sites increases and, in this way, the hydrogenolysis comes into prominence.

The results in this work allow the following conclusions to be formulated:

(i) In aromatization of methylpentane over Ni catalysts both CH_x addition and intramolecular routes appear feasible. One might assume until further proof that the majority of benzene is formed via the C_5 cyclization–ring expansion route. The occurrence of chain lengthening and the apparent ease of the C_5-ring expansion under these hydrogen-deficient conditions might indicate π-bonded, partly dehydrogenated species of C_5 cyclization, i.e., alkyl–alkene (*21*) or carbene–alkene insertion (*2a*). However, the formation of dienic intermediates proposed by Clarke *et al.* (*22, 23*) cannot be excluded.

(ii) The variation of the partial pressure of hydrogen plays an important role in controlling the product selectivity pattern in agreement with observations over Pt (*24, 25*), Rh (*24*), and Pd (*26*). The change of the product distribution under the experimental conditions reported by us can be interpreted by a continuously changing ensemble size caused by the presence of firmly held hydrocarbons. The "carbon effect" which is apparently governed by the partial pressure of hydrogen should be taken into account in the interpretation of the "hydrogen effect" (*24–26*) observed generally in hydrocarbon transformations.

ACKNOWLEDGMENTS

The author is indebted to Dr. J. Volford and Mrs. E. Bursics-Szekeres for synthesizing and purifying the labeled 3-methylpentane, respectively. The author also thanks Professor P. Tétényi for reading the manuscript.

REFERENCES

1. Paál, Z., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 29, p. 273. Academic Press, Orlando, FL, 1980.
2. (a) Gault, F. G., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 30, p. 1. Academic Press, Orlando, FL, 1981; (b) Clarke, J. K. A., and Rooney, J. J., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. 25, p. 125. Academic Press, Orlando, FL, 1976.
3. Amir-Ebrahini, V., and Gault, F. G., *J. Chem. Soc. Faraday Trans. I* **77,** 1813 (1981).
4. Sárkány, A., Pálfi, S., and Tétényi, P., *Acta Chim. Hung. Acad. Sci.* **111,** 633 (1982).
5. Sárkány, A., Tétényi, P., *J. Chem. Soc.* Chem. Commun., p. 525 (1980).
6. Sárkány, A., *J. Catal.* **89,** 14 (1984).
7. Paál, Z., and Tétényi, P., *Nature (London)* **267,** 234 (1977).
8. Ponec, V., and Sachtler, W. M. H., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach (Florida), 1972," p. 654. North-Holland/American Elsevier, Amsterdam, 1973.
9. Anderson, J. R., and MacDonald, R. J., *J. Catal.* **19,** 227 (1970).

10. Anderson, R. J., MacDonald, R. J., Shimoyama, Y., *J. Catal.* **20,** 147 (1971).

11. Schepers, F. J., van Broekhoven, E. H., and Ponec, V., *J. Catal.* **96,** 82 (1985).

12. Guczi, L., Sárkány, A., and Tétényi, P., *J. Chem. Soc. Faraday Trans. I* **70,** 1971 (1974).

13. Sárkány, A., Gaál, J., and Tóth, L., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), Vol. 1, p. 291. Kodansha/Elsevier, Tokyo/Amsterdam, 1981.

14. Sárkány, A., Tétényi, P., *React. Kinet. Catal. Lett.* **12,** 297 (1979).

15. Paál, Z., Dobrovolszky, M., and Tétényi, P., *J. Chem. Soc. Faraday Trans. I* **80,** 3037 (1984).

16. Garin, F., Aeiyach, S., Legare, P., and Maire, G., *J. Catal.* **77,** 323 (1982).

17. Sachtler, W. M. H., *Faraday Disc. Chem. Soc.* **72,** 1 (1981).

18. Van Dijk, W. L., Groenewegen, J. A., and Ponec, V., *J. Catal.* **45,** 277 (1976).

19. Biloen, P., Helle, J. N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63,** 112 (1980).

20. Sárkány, A., *J. Catal.* **97,** 407 (1986).

21. Shephard, F. E., and Rooney, J. J., *J. Catal.* **3,** 129 (1964).

22. Kane, A. F., and Clarke, J. K. A., *J. Chem. Soc. Faraday Trans. I* **76,** 1640 (1980).

23. O'Donohoe, C., Clarke, J. K. A., and Rooney, J. J., *J. Chem. Soc. Faraday Trans. I* **76,** 345 (1980).

24. Paál, Z., and Menon, P. G., *Catal. Rev.* **25,** 229 (1983).

25. Zimmer, H., Dobrovolszky, M., Tétényi, P., and Paál, Z., *J. Phys. Chem.* **90,** 4758 (1986).

26. Paál, Z., and Tétényi, P., *Appl. Catal.* **1,** 9 (1981).