KINETICS OF THE HYDROGENATION OF C_6-C_9 OLEFINS IN THE PRESENCE OF AROMATIC HYDROCARBONS ON A PALLADIUM SULFIDE CATALYST

T. M. Matveeva, N. V. Nekrasov,
M. M. Kostyukovskii, and S. L. Kiperman

UDC 541.127:542.941.7:547.313

The investigation of the main rules governing the selective hydrogenation of olefins in the presence of aromatic hydrocarbons is of great practical and theoretical interest [1]. We have therefore studied the kinetics of hydrogenation of 1-hexene [2]. In the present work this study has been expanded to the hydrogenation of isohexenes with different structures: 1-heptene, 1-octene, and 1-nonene on a palladium sulfide catalyst [3] in the presence of an excess of benzene, toluene, or a mixture of xylenes, and in their absence.

EXPERIMENTAL

The kinetics of the reaction were studied on a flow-through recirculating setup, described in [4]. The tests were carried out in the vapor phase at atmospheric pressure and 40-80°. The olefins were introduced into the system by passing a saturated gas stream (H_2, D_2, He) through thermostated saturators. The characteristics of the catalyst and the conditions for its reduction are given in [2, 3]. The activity of the catalyst was checked periodically by carrying out tests under standard conditions. The composition of the products was determined on a LKhM-8MD chromatograph, using a 5-m column packed with 12% Triton X-303 on Celite 545.

DISCUSSION OF RESULTS

It has been demonstrated in [2] that the hydrogenation of 1-hexane proceeds in the kinetic region. Since the hydrogenation rates of the other olefins studied were found to be the same or lower than the hydrogenation rate of 1-hexene (Fig. 1), it can be assumed that the investigation has been carried out in the kinetic region. The hydrogenation is accompanied by a migration of the double bond along the hydrocarbon chain; the rate of this isomerization was found to be higher than the hydrogenation rate. Skeletal isomerization was not observed under the experimental conditions used.

The kinetic hydrogenation rules were similar for all the C_6-C_9 olefins studied. The shape of the curves representing the hydrogenation rate as function of the degree of conversion (Fig. 2) indicates the absence of reaction inhibition by the product [5]. The reaction rate increases nonlinearily with the increasing partial pressure of the initial substances: the olefin (at a constant H_2 concentration) and H_2 (at a constant olefin concentration) (Figs. 3, 4).

In the presence of aromatic hydrocarbons the hydrogenation rate decreases strongly (Fig. 5), whereby the xylenes inhibit the reaction more strongly than toluene and benzene. Under the reaction conditions the aromatic hydrocarbons remain unchanged. It can be assumed that their influence is based on the competing adsorption of the aromatic and unsaturated hydrocarbons. IR studies have shown that benzene is adsorbed more strongly on the surface of the palladium sulfide catalyst than 1-hexane.

Table 1 shows the influence of replacement of the hydrogen by deuterium in the hydrogenation and isomerization of 2-methyl-2-pentene. Data of the conversion of 1-hexene are also added for comparison [2]. The experiments with H_2 and D_2 were carried out with the same amount of catalyst and similar conversion rates were obtained by varying the volume velocity. The existence of a kinetic isotope effect indicates that the hydrogen participates in the slow stages of both reactions.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya No. 11, pp. 2437-2442, November, 1984. Original article submitted July 12, 1983.

0568-5230/84/3311-2227$08.50

TABLE 1. Kinetic Isotope Effects (β) on Hydrogenation and Isomerization

System	T., °C	Degree of conversion	r, mmole/g·h	β
		Hydrogenation*		
1-Hexene + H_2	80	0,713	717	1,4
1-Hexene + D_2	80	0,703	518	
2-MP-2 + H_2	80	0,661	235	1,6
2-MP-2 + D_2	80	0,692	143	
		Isomerization†		
1-Hexene + H_2	40	0,530	1023	1,5
1-Hexene + D_2	40	0,513	699	
2-MP-2 + H_2	80	0,140	50	1,6
2-MP-2 + D_2	80	0,150	31	

*At equilibrium composition of the isomers.

†The reaction was carried out with a small amount of catalyst (0.01 g), so that the hydrogenation was was negligible.

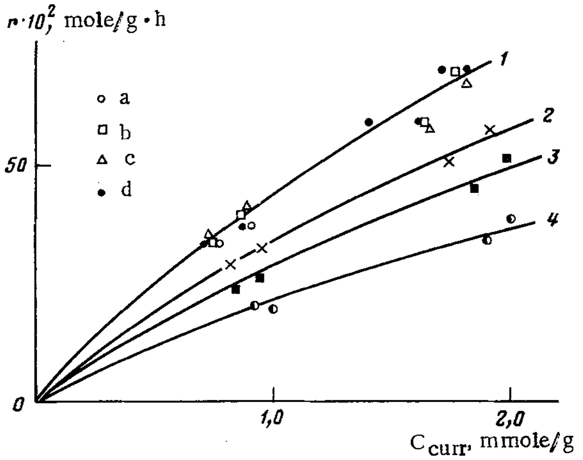

Fig. 1. Hydrogenation rate as function of the the current olefin concentration at 80°: 1) 1-hexene (a); 1-heptene (b); 1-octene (c); 1-nonene (d); 2) 4-M-1-P; 3) 3-M-1-P; 4) 3-M-2-P.

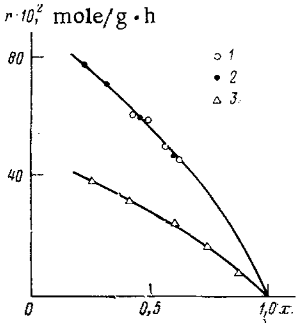

Fig. 2. Hydrogenation rate as function of the degree of conversion; P° = 26.3 gPa, 80°. 1) 1-Hexene; 2) 1-nonene; 3) 4-M-2-P (the solid curves represent the values calculated from Eqs. (1)-(3)).

The hydrogenation and isomerization of olefins in the presence of aromatic hydrocarbons is described by a scheme of stages, analogous to that shown in [2]. It is demonstrated in [2] that the hydrogenation of 1-hexene can be described by the kinetic equation

$$r = \frac{kP_1P_{H_2}}{P_{H_2}^{0.5} + k_1P_1P_{H_2}^{0.5} + k_2P_1 + k_bP_b + k_tP_t + k_xP_x} \qquad (1)$$

where P_1, P_{H_2}, P_b, P_t, P_x are the partial pressures of the olefin, H_2, benzene, toluene, and the equilibrium mixture of xylenes respectively; k, k_1, k_2, k_b, k_t, k_x are constants which

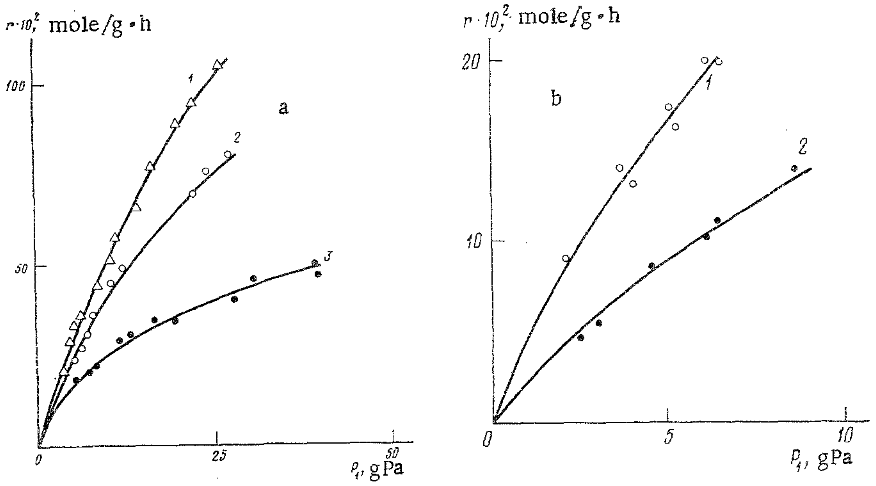

Fig. 3. Hydrogenation rate as function of the current partial pressure of the olefin at the temperature, °C, 1-hexene (a): 1) 80; 2) 60; 3) 40°; 2-M-2-P (b): 1) 80; 2) 40° (solid curves calculated from Eqs. (1)-(3)).

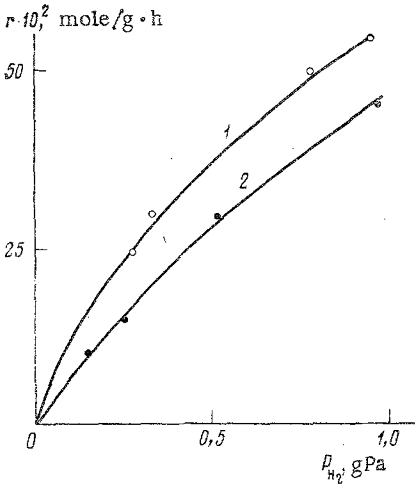

Fig. 4. Hydrogenation rate as function of the partial pressure of H_2 at 80°: 1) 1-hexene; 2) 4-M-2-P (solid curves calculated from Eqs. (1)-(3)).

include the adsorption coefficients. The values of the constants are given in Table 2. Since the rules governing the hydrogenation of olefins were found to be similar, their hydrogenation rates can be described by Eq, (1).

In the separate hydrogenation of 4-methyl-2-pentene, 2-methyl-1-pentene, and 2-methyl-2-pentene mixture of all three isomers actually take part in the process, due to rapid isomerization, regardless of the fact which of them had been the initial one. Although isomerization proceeds more rapidly than hydrogenation, an equilibrium was not reached in isomerization; this allowed us to vary the ratio between the isomers by chosing one of them as the initial olefin. This allowed us to determine the rates of hydrogenation and isomerization of each of the methylpentenes separately. In this case the hydrogenation rate of each of the methylpentenes is given by the kinetic equations

$$r_1 = \frac{(k_1P_1 + k_2P_2 + k_3P_3)\,P_{H_2}}{M} \tag{2}$$

$$M = P_{H_2}^{0.5} + (k_4P_1 + k_5P_2 + k_6P_3)\,P_{H_2}^{0.5} + k_7P_1 + k_8P_2 + k_9P_3 + \\ + k_bP_b + k_tP_t + k_xP_x\,. \tag{3}$$

TABLE 2. Constants for Eq. (1)

T., °C	$k \cdot 10^2$, mole/g·h·gPa$^{1.5}$	k_1, gPa^{-1}	k_2	k_b	k_t	k_x
			gPa$^{-0.5}$			
40	0,148	0,113	0,461	2,67	4,02	11,3
60	0,185	0,022	0,571	1,28	2,10	6,1
80	0,225	0,005	0,690	0,67	1,18	2,9
E*, kJ/mole	9,6	−71,1	9,2	−31,1	−28,4	−31,7

*Activation energy or parameter which characterizes the temperature dependence of the constants.

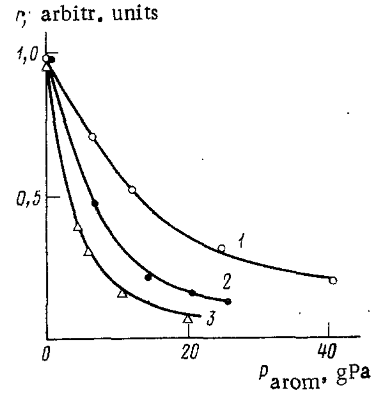

Fig. 5. Hydrogenation rate of methylpentenes as function of the amount of aromatic compounds added at 80°: 1) benzene; 2) toluene; 3) equilibrium mixture of xylenes (solid curves calculated from Eqs. (1)-(3)).

where P_1, P_2, P_3 are the partial pressures of 4-methyl-2-pentene (4-M-2-P), 2-methyl-2-pentene (2-M-2-P), and 2-methyl-1-pentene (2-M-1-P) respectively.

The accumulation rate of each methylpentene in the case of simultaneous hydrogenation and isomerization is given by the equations

$$r_{4\text{-MP-2}} = \frac{(k_{10}P_2 - k_{11}P_1)\,P_{H_2}^{0.5} - k_1P_1P_{H_2}}{M} \tag{4}$$

$$r_{2\text{-MP-2}} = \frac{(k_{11}P_1 - k_{10}P_2)\,P_{H_2}^{0.5} - k_2P_2P_{H_2} - (k_{12}P_2 - k_{13}P_3)\,P_{H_2}^{0.5}}{M} \tag{5}$$

$$r_{2\text{-MP-1}} = \frac{(k_{12}P_2 - k_{13}P_3)\,P_{H_2}^{0.5} - k_3P_3P_{H_2}}{M} \tag{6}$$

The rates were calculated from the kinetic equations (1)-(6) on a BÉSM-6 computer, using a modified FUMILI program and the values of the constants given in Tables 2 and 3. The mean-square deviation of the calculated data from the experimental ones was 19-22%. The confidence interval of the calculated constants of Eqs. (1)-(6) with a probability of 95% was equal to ±15%.

The kinetic equations (2) and (3) describe hydrogenation of mixtures of different compositions. In order to extend this kinetic model to other mixtures, we have prepared synthetic blends with different compositions. By assuming a simple interaction, i.e., adsorptive displacement of one component of the reaction mixture by another from the catalyst surface and by applying the above equations for individual hydrogenations, the hydrogenation rates of, for instance, mixtures of 1-hexene and 1-nonene can be expressed by

TABLE 3. Constants for Eqs. (2)-(6)*

T., °C	$k_1 \cdot 10^2$	$k_2 \cdot 10^2$	$k_3 \cdot 10^2$	k_4	k_5	k_6	k_{10}	k_{11}	k_{12}	k_{13}	k_b	k_t	k_x
	mole/g · h · gPa$^{1.5}$			gPa^{-1}			10^2 · mole/g · h · gPa$^{1.5}$				gPa$^{-0.5}$		
40	0,059	0,043	0,087	0,038	0,016	0,038	0,67	3,0	0,53	1,7	1,9	3,9	13,0
60	0,098	0,070	0,110	0,038	0,020	0,038	0,87	3,5	0,77	2,6	2,0	3,9	13,0
80	0,150	0,110	0,150	0,038	0,025	0,038	0,10	4,1	1,10	3,7	2,0	3,9	13,0
E, kJ/mole	21,7	20,9	17,1	0	10,0	10,0	11,7	7,5	16,3	17,1	1,3	0	0

*Calculations have shown that the values of constants k_7, k_8, and k_9 are small; they can therefore be neglected.

TABLE 4. Simultaneous Hydrogenation of a Binary Mixture of 1-Hexene and 1-Nonene at 80°

$\overset{\circ}{P}_{C_6}$	$\overset{\circ}{P}_{C_9}$	x_{C_6}	x_{C_9}	P_{C_6}	P_{C_9}	$r \cdot 10^2$, mole/g · h					
						C_6			C_9		
gPa				gPa		experimental	calculated from Eqs.		experimental	calculated from Eqs.	
							(1)	(7)–(9)		(1)	(7)–(9)
39,5	26,3	0,20	0,24	31,5	19,9	58,7	70,2	52,4	46,8	55,4	33,2
26,3	26,3	0,29	0,32	18,6	17,9	36,9	53,9	38,7	40,4	52,6	37,2
13,2	26,3	0,21	0,22	10,5	20,4	19,4	37,2	24,2	41,9	57,4	47,0
26,3	13,2	0,69	0,78	8,0	3,0	26,6	30,6	28,2	15,0	13,2	10,4
26,3	39,5	0,63	0,63	9,9	14,6	24,7	34,8	25,0	37,4	45,9	37,1

$$r_{C_6} = \frac{k_{C_6} P_{C_6} P_{H_2}}{M'} \quad (7)$$

$$r_{C_9} = \frac{k_{C_9} P_{C_9} P_{H_2}}{M'} \quad (8)$$

$$M' = P_{H_2}{}^{0.5} + (k_{C_6}{}' P_{C_6} + k_{C_9}{}' P_{C_9}) P_{H_2}{}^{0.5} + k_{C_9}{}'' P_{C_9} + k_{C_6}{}'' P_{C_6} \quad (9)$$

where the constants, k_{C_6}, k_{C_9}, k_{C_6}', k_{C_9}', k_{C_6}'', k_{C_9}'' have the same meaning as those given in Table 2 for the hydrogenation of individual components C_6-C_9. The items in the denominator indicate adsorption inhibition by both components.

The hydrogenation rates calculated from Eqs. (1) and (7)-(9) are given in Table 4. The mean square deviation of the experimental data from those calculated from Eq. (1) was found to be 30%, the deviation of those calculated from Eqs. (7)-(9) 22%. The good agreement between these values (derived from Eqs. (7)-(9)) indicates that the assumption of a simple interaction mechanism is correct.

Thus, the simple interaction is described by kinetic equations of the same kind as in the case of individual hydrogenation, only introducing a more complicated denominator due to competitive adsorption. It is essential that no new constants are required to describe simultaneous hydrogenation rates; they are all obtained in separate hydrogenation tests.

CONCLUSIONS

1. A kinetic model has been established for the hydrogenation of C_6-C_9 olefins on a palladium sulfide catalyst at atmospheric pressure in the presence of benzene, toluene, and xylenes, according to which the aromatic hydrocarbons inhibit the reaction due to adsorptive displacement.

2. When hydrogen is replaced by deuterium, kinetic isotope effects are observed in hydrogenation as well as in isomerization; this indicates the participation of hydrogen in the slow stages of both reactions.

3. The hydrogenation rates of the individual olefins in mixtures can be calculated on the basis of constants determined in the investigation of the individual olefins, i.e., simple interactions take place in the system.

LITERATURE CITED

1. A. B. Vol'-Épshtein, A. A. Krichko, and T. N. Mukhina, Composition and Processing of Liquid Pyrolysis Products, Thematic Review. Series on Petrochemistry and Shale Processing [in Russian], TsNIITÉNeftekhim, Moscow (1969).
2. T. M. Matveeva, N. V. Nekrasov, M. M. Kostyukovskii, M. D. Navalikhina, A. A. Krichko, and S. L. Kiperman, Izv. Akad. Nauk SSSR, Ser. Khim., 1243 (1982).
3. Kh. M. Minachev, M. A. Ryashchentseva, and A. M. Rubinshtein, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 820 (1959).
4. A. A. Andreev and S. L. Kiperman, Kinet. Katal., 6, 869 (1965).
5. G. S. Bashkirova and S. L. Kiperman, Kinet. Katal., 11, 631 (1970).