MECHANISM OF THE AROMATIZATION OF n-HEXANE ON ALUMINA—PLATINUM

CATALYSTS WITH ADDITIONS OF CADMIUM AND RHENIUM

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The aromatization of paraffins on Pt catalysts can take place by three different routes: 1) dehydrogenation of the paraffins through olefins and dienes to trienes followed by their cyclization to cyclohexadienes and dehydrogenation to aromatic hydrocarbons; 2) through the intermediate formation of alkylcyclopentanes and dehydroisomerization (DHI) to aromatic hydrocarbons; and 3) direct cyclization of the paraffins to six-membered napthenes and subsequent dehydrogenation.

The aromatization of hexane on AP-64 reforming alumina—platinum catalyst (APC) as been studied previously by the kinetic isotope method (KIM) [1] and it has been shown that the main intermediates of the reaction are hexane and methylcyclopentane (MCP) [2]. It is known [3] that the additions of Re and Cd used for modifying APCs substantially increase the specific surface of the Pt. The introduction of Cd raises the selectivity of aromatization by suppressing the side reaction of hydrocracking [4]. To investigate the influence of additions of Re and Cd on the mechanism of aromatization of paraffins, we have studied the role of hexenes and methylcyclopentane in the aromatization of n-hexane on Pt—Re/Al$_2$O$_3$ and Pt—Cd/Al$_2$O$_3$ catalysts with the aid of the kinetic isotope method. The properties of these catalysts have been compared with the properties of the AP-64 catalyst.

EXPERIMENTAL

The experiments were performed in a pulsed radiochromatographic apparatus in a current of H$_2$ at 550°C and a pressure of 1.25 atm gauge. The experimental procedure and conditions of analyzing the reaction products have been described previously [2].

The catalysts contained 0.36% of Pt and 0.2% of Re/Al$_2$O$_3$ (sample 1), and 0.36% of Pt and 0.5% of Cd/Al$_2$O$_3$ (sample 2).

DISCUSSION OF RESULTS

In addition to hexane, we studied the conversion of possible intermediates in the aromatization process: hex-1-ene, hexa-1,3-diene, methylcyclopentane, 2-methylcyclopentene (2-MCPene), methylcyclopentadienes (MCPdienes) and cyclohexane (CH). The results obtained (Table 1) show that the replacement of the initial hexane by hexene and then by hexadiene leads to some increase in the yield of benzene. Such a situation is in harmony with the occurrence of the reaction by the successive dehydrogenation of the paraffin. A considerable part of the unsaturated hydrocarbons is consumed in hydrogenation and hydrocracking reactions. Thus, under these conditions hex-1-ene gave 60.9% of hexanes, while hexa-1,3-diene gave 60% of hexanes and hexenes and less than 0.5% of hexadiene was left.

In addition to aliphatic hydrocarbons, hydrocarbons of the cyclopentane series, namely methylcyclopentane, methylcyclopentenes, and methylcyclopentadienes, may also take part in the aromatization reaction. They are not only formed from alkanes and alkenes but themselves are converted into benzene. At the same time, a slight fall in the yield of benzene is observed with a rise in the degree of unsaturation of the cyclic hydrocarbon, which is possibly connected with the participation of the unsaturated compounds in other reactions. Since the yields of linear products of the hydrogenolysis of methylcyclopentane, methylcyclopentene, and methylcyclopentadienes are comparatively small and they are incapable of ensuring the

TABLE 1. Results of Experiments on the Conversion of Individual Hydrocarbons on Pt-Re/Al$_2$O$_3$ (15 mg, 500°C, H$_2$ 60 ml/min

Initial hydro-carbon	Amount in the catalysate, %							
	cracking product	isohexanes	hexane	hexenes	MCP	MCPenes	MCPdienes + hexadienes	benzene
Hexane	11,74	10,37	55,12	6,35	5,45	1,80	0,13	8,69
Hex-1-ene	14,04	13,65	47,26	6,33	5,90	2,35	0,34	9,87
Hexa-1,3-diene	18,09	12,74	41,27	5,45	6,40	2,51	0,34	13,20
MCP	3,77	7,88	4,01	1,75	48,07	11,50	4,03	13,43
2-MCPene	4,61	8,61	4,33	1,88	45,71	17,85	4,71	12,00
MCPdienes	7,16	7,89	3,83	6,97	39,40	17,25	5,30	11,98

TABLE 2. Results of Experiments with a Mixture of Hexane and [^{14}C]Hex-1-ene (11.5%) on Pt-Re/Al$_2$O$_3$ and Pt-Cd/Al$_2$O$_3$ Catalysts (550°C, H$_2$ 60 mg/min)

Weight of catalysts, mg	Amount in the catalysate, %								
	cracking product	isohexanes	hexane	hexenes	MCP	1-MCPene	MCPdienes	hexadienes+2- and 3-MCPenes	benzene
	Pt-Re/Al$_2$O$_3$								
0,5	2,6	0,5	80,4	12,7	0,5	0,4	0,5	1,1	1,4
1,0	3,6	1,4	73,5	13,5	0,8	0,9	1,0	2,0	3,3
2,0	4,2	3,3	66,0	13,7	1,9	1,5	1,3	3,0	5,1
3,0	6,0	5,8	56,3	13,4	2,4	1,7	1,7	3,3	9,4
4,0	8,0	6,2	52,9	12,7	2,6	1,9	1,8	3,4	10,7
	Pt-Cd/Al$_2$O$_3$								
1,0	3,0	1,1	75,5	12,4	0,8	1,1	1,1	2,0	3,0
2,0	3,8	2,5	67,2	13,0	1,8	1,6	1,7	3,0	5,6
3,0	5,2	4,1	58,7	12,9	2,6	2,1	2,3	3,5	9,2
4,0	6,7	5,1	53,0	12,1	3,1	2,5	2,7	3,5	11,3

observed rate of aromatization through subsequent dehydrogenation of the hexane and hexene formed, it is obvious that the formation of benzene from five-membered rings is due mainly to the occurrence of a dehydroisomerization reaction.

To estimate the contribution of hexenes to the overall mechanism of the formation of benzene, we passed a mixture of hexane and of [^{14}C]hex-1-ene over both catalysts at various contact times. As can be seen from Table 2 and Fig. 1, there were no great differences in the nature of the action of these catalysts. Thus, at the same weights of the samples the yields of benzene practically coincided, and the catalysates contained approximately equal amounts of hexane and hexenes; the molar radioactivities (MRAs) of the hexane and benzene were also close, and only for the hexene did they differ somewhat.

The appearance of the radioactive label in the benzene unambiguously shows the participation of the hexene in the aromatization reaction. A marked decrease in the molar radioactivity of the hexene with an increase in the time of contact indicates a high rate of the hydrogenation of hexane. It can be seen that with a 4-mg sample of any catalyst the molar radioactivity of hexene amounts to ~20% of the initial value and, therefore, the initial hexene was diluted fivefold, although according to Table 2 the amount of hexene in the catalysate scarcely changed, which is connected with its subsequent transformations. The passage of radioactivity into hexane shows the occurrence of the hydrogenation of the hexene, which is in harmony with Table 1.

Since the experimental curve of the molar radioactivity of benzene in Fig. 1 is located between the curves for hexane and for hexene, the participation of olefins in aromatization can be represented by a triangular scheme (1)

$$\text{Hexane} \underset{W_1'}{\overset{W_1}{\rightleftarrows}} \text{Hexene}$$
$$W_3 \searrow \qquad \swarrow W_2$$
$$\text{Benzene}$$

(1)

TABLE 3. Rates of Conversion
of Hexane and Hexene in Experiments with Mixtures of Hexane —
$[C^{14}]$Hex-1-ene (rel. units)

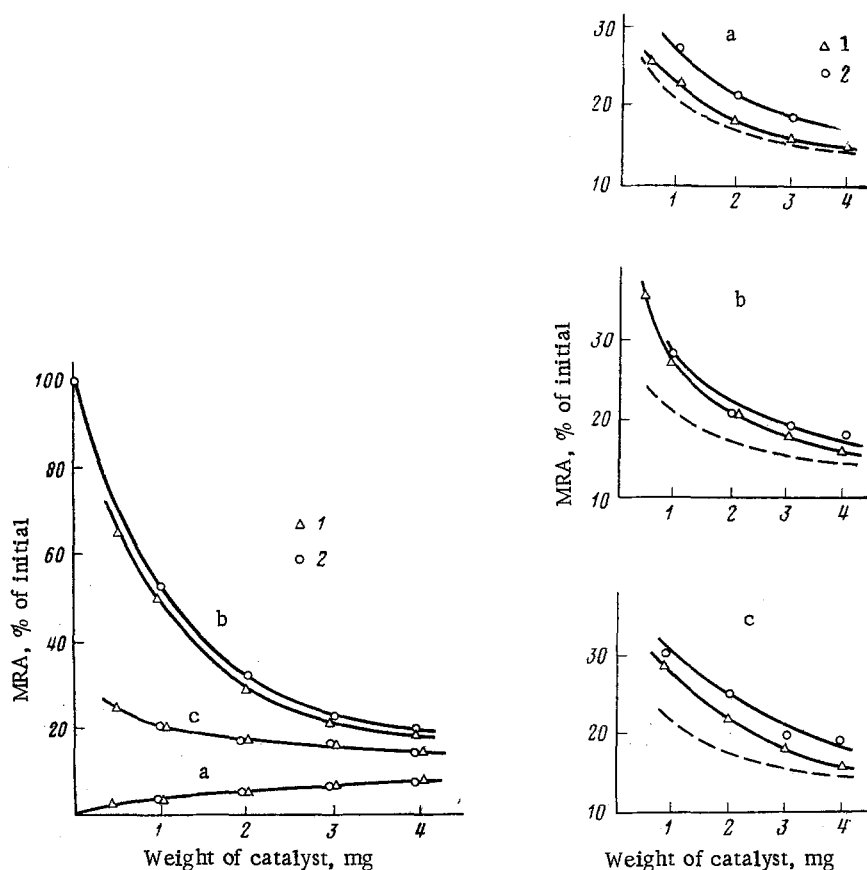| Weight, mg	W_1	$W_{1'}$	W_2	W_3
	Pt–Re/Al$_2$O$_3$			
1,0	8,46	4,21	0,91	2,04
2,0	6,46	4,42	0,97	1,98
3,0	4,77	4,36	0,89	2,06
	Pt–Cd/Al$_2$O$_3$			
1,0	7,08	3,92	0,84	2,18
2,0	5,35	3,98	0,87	2,15
3,0	4,00	3,94	0,94	2,08

Fig. 1   Fig. 2

Fig. 1. Dependence of the molar radioactivities of hexane
(a), hexene (b), and benzene (c) on the weight of catalyst
in experiments with a mixture of hexane and [^{14}C]hex-1-ene
(11.5%) on Pt–Re/Al$_2$O$_3$ (1) and Pt–Cd/Al$_2$O$_3$ (2) catalysts.

Fig. 2. Dependence on the molar radioactivities of methyl-
cyclopentane (a), methylcyclopentenes (b), and methylcyclo-
pentadienes (c) on the weights of catalyst in experiments
with hexane–[^{14}C]hex-1-ene (11.5%): 1) Pt–Re/Al$_2$O$_3$; 2)
Pt–Cd/Al$_2$O$_3$; dashed line — molar radioactivity of benzene.

where W_i represents the rate of an individual stage of the reaction. Calculation of these
rates of the stages for the two samples of catalysts was carried out on the basis of the
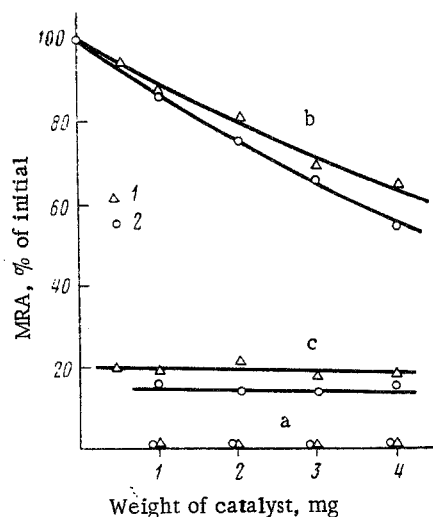
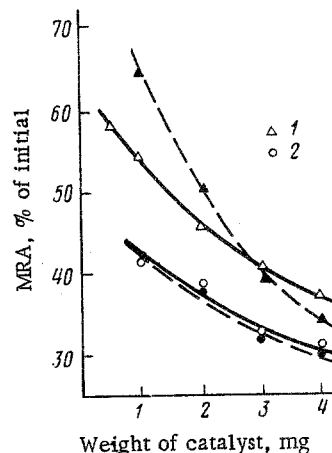Fig. 3   Fig. 4

Fig. 3. Dependence of the molar radioactivities of hexane
(a), of methylcyclopentane (b), and of benzene (c) on the
weight of catalyst in experiments with a mixture of hexane
and [^{14}C]methylcyclopentane(8.5%): 1) Pt—Re/Al$_2$O$_3$; 2)
Pt-Cd/Al$_2$O$_3$.

Fig. 4. Dependence of the molar radioactivities of methyl-
cyclopentenes (full curves) and methylcyclopentadienes
dashed curves) on the weight of catalyst in experiments with
a mixture of hexane and [^{14}C]methylcyclopentane: 1) Pt—Re/
Al$_2$O$_3$; 2) Pt—Cd/Al$_2$O$_3$.

equations for the kinetic isotope method [1]. The results of the calculation, which are given
in Table 3, show that for both samples W_3 was twice W_2, i.e., the aromatization of hexane
can take place at an appreciable rate even without the participation of hexene. Since the
values of W_2 and W_3 differed little from the two samples, it may be assumed that the compo-
sition of the catalyst does not appreciably affect the degree of participation of hexene in
the formation of benzene. Integration of the rates with respect to the time of the contact
enabled us to show that only 1/3 of the benzene is formed with the participation of olefins
desorbed into the gas phase and, as on AP-64 catalyst [2], the bulk of it is formed by a
route determined by the rate W_3.

It can be seen from Table 3 that the rates of interconversion of hexane and hexene (W_1
and W_1') several times exceed the rate of aromatization, which is apparently the reason for
the rapid convergence of the molar radioactivities of the hexenes and of hexane with an in-
crease in the time of contact.

Some differences between the samples of catalyst can be seen from Table 2 and Fig. 2.
On sample 2 the yield of all hydrocarbons with five-membered rings (see Table 2) was greater,
and the difference in the yields of the hydrocarbons methylcyclopentane, methylcyclopentene,
and methylcyclopentadiene rose in this sequence on both catalysts. Since cyclopentane hydro-
carbons can act as intermediates in the aromatization of hexane, it is quite possible that
the addition of Cd leads to an inhibition of the dehydroisomerization reaction and, conse-
quently, to an accumulation in the catalysate of hydrocarbons with five-membered rings. The
appreciable molar radioactivities of all the C$_5$-cyclic hydrocarbons shows the participation
of hexenes not only in benzene-formation but also in the C$_5$-dehydrocyclization (C$_5$-DHC) re-
action.

As can be seen from Fig. 2, the molar radioactivities of all the C$_5$-cyclic hydrocarbons
were either equal to that of benzene or somewhat exceeded it. Consequently, the contribution
of the hexenes to the C$_5$-dehydrocyclization reaction is not less than to the aromatization
reaction, although the route of the direct conversion of hexane into C$_5$-cyclic hydrocarbons
is not excluded, either.

It can be seen from Table 2 that such processes as hydrocracking and skeletal isomer-
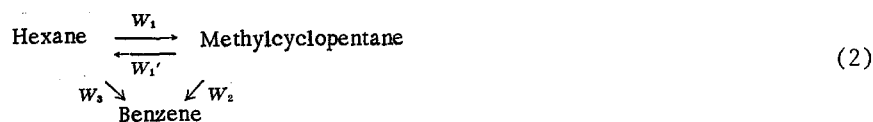
TABLE 4. Results of Experiments with a Mixture of Hexane and [^{14}C]Methylcyclopentane (8.5%) on Pt–Re/Al$_2$O$_3$ and Pt–Cd/Al$_2$O$_3$ Catalysts (550°C, H$_2$ 60 ml/min)

Weight of catalyst, mg	Amount in the catalysate, %								
	cracking product	isohexanes	hexane	hexenes	MCP	1-MCP-ene	MCPdi-enes	hexadienes + 2- and 3-MCPenes	benzene
Pt–Re/Al$_2$O$_3$									
0,5	1,0	0,5	83,5	4,2	7,9	0,7	0,5	0,7	1,2
1,0	1,8	1,1	76,5	7,2	7,2	1,2	1,0	1,6	2,6
2,0	2,3	2,5	67,4	10,6	6,5	2,0	1,8	2,5	4,5
3,0	4,5	4,2	58,1	11,5	6,0	2,4	2,4	2,4	8,5
4,0	5,5	4,8	53,8	11,6	5,7	2,5	2,6	3,0	10,3
Pt–Cd/Al$_2$O$_3$									
1,0	1,8	0,8	77,1	5,8	7,5	1,3	1,3	1,5	3,1
2,0	2,1	2,1	67,1	9,7	6,6	2,1	2,2	2,7	5,4
3,0	3,8	3,3	59,4	10,2	6,1	2,5	2,7	3,5	9,0
4,0	4,3	4,0	54,8	10,9	6,3	2,8	2,9	3,6	10,3

ization in the presence of Pt–Cd/Al$_2$O$_3$ take place at a lower rate than on Pt–Re/Al$_2$O$_3$. Since these reactions, like dehydroisomerization, take place with the participation of the acidic centers of the alumina–platinum catalysts, the action of Cd can to some extent be compared with the action of an alkaline additive which suppresses processes of the acid–base type.

In order to estimate the contribution of the dehydroisomerization of five-membered rings to the aromatization of hexane, we performed experiments with a binary mixture of hexane and of [^{14}C]methylcyclopentane. The results of a radiochromatographic analysis of the catalysate are given in Table 4 and in Figs. 3 and 4. The yields of benzene and the amounts of hexane in the catalysates on identical weights of catalysts coincide within the limits of experimental error. However, the yields of methylcyclopentene and of methylcyclopentadiene on sample 2 were considerably higher than on sample 1. The opposite pattern is observed for cracking products and for isohexanes.

The decrease in the molar reactivity of the methylcyclopentane with an increase in the time of contact (see Fig. 3), and also the appearance of radioactivity in the benzene, is evidence that methylcyclopentane is an aromatization intermediate. Since for sample 2 the curve of the molar radioactivity of methylcyclopentane runs somewhat more steeply, the initial [^{14}C]methylcyclopentane apparently underwent greater dilution in the presence of Pt–Cd/Al$_2$O$_3$. This result may indicate that sample 2 possesses a greater activity in relation to C$_5$-dehydrocyclization. However, it is more probable that, as already mentioned, the dehydroisomerization reaction is inhibited on this catalyst and therefore an accumulation of methylcyclopentane takes place (see Table 4). This is also confirmed by the fact that the benzene formed on sample 2 possessed a smaller molar radioactivity than on sample 1, i.e., the contribution of methylcyclopentane to the formation of benzene (through dehydroisomerization) was less on Pt–Cd/Al$_2$O$_3$.

$$\text{Hexane} \underset{W_1'}{\overset{W_1}{\rightleftharpoons}} \text{Methylcyclopentane}$$
$$W_3 \searrow \qquad \swarrow W_2$$
$$\text{Benzene} \qquad (2)$$

The rates obtained from the equations of the kinetic isotope method for Scheme (2) (Table 5) also confirm the fact that Pt–Re/Al$_2$O$_3$ possesses a somewhat higher activity in the dehydroisomerization reaction, while on this catalyst C$_5$-dehydrocyclization takes place at a lower rate than on Pt–Cd/Al$_2$O$_3$. By integrating the rates W_2 and W_3 with respect to the time of contact it was found that the contribution of methylcyclopentane to the formation of benzene on sample 1 was ~20% and on sample 2 it was ~15%.

Thus, the total contribution of hexenes and methylcyclopentane to the aromatization of hexane on the catalysts studied does not exceed 55%. These results agree well with those obtained for AP-64 catalyst [2].

As can be seen from Fig. 4, the molar radioactivities of methylcyclopentane and methylcyclopentadiene were considerably less than that of methylcyclopentane. These products are

TABLE 5. Rates of Conversion
of Hexane and of Methylcyclo-
pentane in Experiments with a
Mixture of Hexane and [^{14}C]-
Methylcyclopentane (arbitrary
units)

Weight, mg	W_1	W_1'	W_2	W_3
Pt–Re/Al$_2$O$_3$				
1,0	0,80	0,07	0,54	2,04
2,0	0,75	0,07	0,57	1,97
3,0	0,72	0,07	0,60	1,98
Pt–Cd/Al$_2$O$_3$				
1,0	1,08	0,07	0,46	2,27
2,0	0,88	0,07	0,47	2.26
3,0	0,76	0,07	0,47	2.26

apparently obtained not only by the dehydrogenation of methylcyclopentane but also directly from the aliphatic hydrocarbons (for the molar radioactivity of methylcyclopentane, see Fig. 3).

In order to check the possibility of the occurrence of the reaction through a stage of the formation of a C$_6$-naphthene, a ternary mixture of hexane, [^{14}C]hex-1-ene (10%), and cyclohexane (30%) was passed over a catalyst. The results of these experiments showed that the label does not pass into the cyclohexane, i.e., it may be considered that this hydro-carbon is not formed under the reaction conditions and is not an intermediate in the aroma-tization of hexane.

Thus, the results obtained permit the conclusion that on the multicomponent catalysts studied and on AP-64 alumina–platinum catalyst the mechanisms of the aromatization of paraf-fins are identical. There are two reaction pathways: 1) the successive dehydrogenation of the initial alkane through olefins, dienes, etc.; and 2) with the intermediate formation of five-membered rings. The fact that according to calculations by the kinetic isotope method the two pathways do not ensure the total formation of benzene is, as reported previously [2], apparently connected with the fact that the desorption of the intermediates takes place more slowly than their subsequent conversion on the surface of the catalyst.

The addition of Re and Cd, without affecting the overall mechanism of the aromatization of hexane, has some influence on the ratio of the two routes of aromatization. This is because the addition of CD somewhat decreases the acid–base function of the catalyst, pro-moting the dehydroisomerization of the five-membered rings and also the occurrence of hydro-cracking and isomerization reactions.

SUMMARY

1. The influence of additions of Re and Cd to an alumina–platinum catalyst on the mechanism of the aromatization reaction has been studied with the aid of the kinetic isotope method.

2. The formation of benzene from hexane on alumina–platinum catalysts with addition of Re and Cd takes place with the participation both of hexene and of methylcyclopentane. Cyclo-hexane is not formed under the reaction conditions.

3. Additions of Re and Cd do not appreciably change the routes of the aromatization of n-hexane. The addition of Cd somewhat inhibits the reactions taking place on the acidic centers of the catalyst — in particular, the dehydroisomerization of five-membered rings to aromatic systems. Consequently, the introduction of Re and Cd somewhat changes the relative roles of each of the routes mentioned in the overall benzene-forming process.

4. On alumina–platinum catalysts, hexenes participate not only in aromatization but also in the C$_5$-dehydrocyclization reaction, the contributions of the hexenes to the two reactions being comparable.

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ACTIVATION OF MOLECULAR HYDROGEN BY TRANSITION-METAL COMPLEXES.

4. KINETICS OF HYDROGENATION OF SALICYLALDEHYDE CATALYZED BY

A PALLADIUM CLUSTER

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A cluster of composition $(PPh)_2Pd_5$ (I) catalyzes the hydrogenation of dienes, monoenes, acetylenes, nitro compounds, nitroso compounds, azo compounds, Schiff bases, organic peroxides, and quinones at 20°C and 1 atm [1]. To obtain information on the reactivity of (I), we investigated the kinetics of reduction of salicylaldehyde (S) in solutions of (I) in DMFA.

EXPERIMENTAL

Salicylaldehyde was purified by distillation in vacuo. DMFA of cp grade was used without additional purification.

The experiments were carried out as follows: a solution of (I) in DMFA was degassed by vacuum treatment, H_2 was passed into the solution, and the aldehyde was added in the H_2 stream. The reaction kinetics was studied with a volumetric setup at 1 atm and 20°C. By special experiments, it was shown that with stirring of the solution with a magnetic stirring device, the reaction proceeded in the kinetic region. The error in the determination of the rate constants was ≤10%.

The catalyzate was analyzed by GLC (LKhM-8MD chromatograph, 2-m × 0.03-m column, Apiezon on Chromaton, carrier-gas velocity of 30 ml/min, and internal standard of phenol).

The relation of the concentration of H_2 in DMFA to P_{H_2} was taken from [2]. The formation of the complex between (I) and S was investigated colorimetrically [FÉK-56 M, λ 600 nm, cuvette thickness of 3 mm, and solution of (I) in the reference cuvette]. The error in the determination of the equilibrium constant was ≤30%.

DISCUSSION OF RESULTS

At 20°C and 1 atm, the solution of (I) in DMFA did not absorb H_2 (with a precision of ±0.1 mole H_2/g-atom of Pd) and did not change coloration in an atmosphere of H_2. When S was added to the solution of (I), the absorbance increased at 600 nm, indicating the formation of a complex of (I) with S

$$(I) + S \underset{k_{-1}}{\overset{k_1}{\longrightarrow}} (I \cdot S) \tag{A}$$

Treatment of the obtained data according to the method of [3] (Fig. 1) gave a value of the equilibrium constant for reaction (A), K_1, of 140 liters/mole.