ADSORPTION AND HYDROGENATION OF BENZENE ON Pd-Ru ALLOY

IN A PULSED CHROMATOGRAPHIC REGIME

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The amount of hydrogen in Pd alloys substantially affects their adsorption and catalytic properties [1]. In a study of the adsorption of cyclohexane (CH) vapors on the walls of a capillary made from an alloy of Pd with 6% of Ru, it was found [2] that hydrogen-poor and hydrogen-rich phases of this alloy differed greatly with respect to the influence of partial pressure of H_2 on the adsorption of CH. In the present investigation, using the pulsed chromatographic method [3], we have studied the adsorption and hydrogenation of benzene in the same capillary at various amounts of hydrogen in the alloy and with different methods of feeding the hydrogen: in a mixture with benzene vapor, and by diffusion through the walls of the capillary.

EXPERIMENTAL

The apparatus and procedure for performing the experiments have been described previously [2]. The benzene hydrogenation products were analyzed in a column 1 m long with a diameter of 1 mm filled with Resorb C impregnated with 10% of PEGA. At 303°K, strongly adsorbed benzene occupies ~7% of the surface of the internal walls of a capillary made from Pd-Ru alloy, as was determined from the isotherm of the reversible adsorption benzene shown by curve 1 in Fig. 1. This isotherm is satisfactorily described by the Langmuir equation. In the absence of hydrogen, no benzene transformation products were detected.

In the presence of hydrogen, benzene was hydrogenated to CH. To exclude the transfer of hydrogen through the walls of the capillary currents of mixtures of nitrogen and hydrogen of the same composition bathed its internal and external walls simultaneously. The intermediate hydrogenation products — cyclohexadiene and cyclohexene — were not detected at a sensitivity of gas-chromatographic analysis of $5 \cdot 10^{-10}$ mole.



Fig. 1. Isotherms of the reversible adsorption of benzene vapor on the walls of a Pd—Pu alloy capillary in the absence of hydrogen on the β phase of the alloy—hydrogen system (1) and on the α phase at $P_{H_2} = 1$ torr (2).

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Fig. 2

Fig. 3

Fig. 2. Elution curves obtained with a feed of benzene to the α phase of the alloy-hydrogen system (P_{H₂} = 1 torr: rate of flow of the carrier gas 1.2 ml/min).

Fig. 3. Elution curves of the reactants obtained with a feed of benzene to the β phase of the alloy-hydrogen system (P_{H2} = 70 torr; rate of flow of carrier gas 1.2 ml/min): 1) C₆H₁₂ formed; 2) unchanged C₆H₆; 3) 1 + 2; 4) C₆H₆ + C₆H₁₂ immediately after the reactor. Curves 1-3 were obtained from experiments using a supplementary column. The points [a) C₆H₁₂ formed; b) unchanged C₆H₆] were obtained from experiments with freezing out.

DISCUSSION OF RESULTS

The elution curves obtained when pulses of a mixture of benzene and methane vapors in a stream of nitrogen-hydrogen mixture in which the partial pressure of H₂ was 1 torr were fed into the capillary are shown in Fig. 2. Under these conditions the α phase of the alloy-hydrogen system exists [2]. The pulses corresponding to elution curves 1-3 contained 1.13^o 10⁻⁷, 0.57 · 10⁻⁷, and 0.29 · 10⁻⁷ mole of benzene, respectively (ratio 3.93:1.95:1); the amounts of CH formed, determined in parallel experiments with the freezing out of the issuing hydrocarbon followed by chromatographic analysis, were 1.03 · 10⁻⁸, 0.96 · 10⁻⁸, and 0.84 · 10⁻⁸ mole, respectively (ratio 1.15:1.09:1). The peak marked C₆H₁₂ (2) relates to CH, and that marked C₆H₆ to benzene. The ratio of the amounts of CH formed shows that the order of the reaction with respect to benzene was close to zero.

With an increase of P_{H_2} in the gas phase and passage to the region of existence of the β phase in the alloy-hydrogen system [2], the benzene and CH issuing form the capillary were not separated and formed a single peak (Fig. 3, curve 4). In order to be able to separate the benzene and CH in an issuing pulse and to determine the residence time of each of them, two methods were used. The first of them consisted in passing the outlet pulses corresponding to one and the same inlet pulse through a trap which could be rapidly cooled with liquid nitrogen. The moment of freezing was selected in such a way that part of the pulse passed directly into a supplementary column without freezing and the remainder of the pulse was retained in the trap and was analyzed separately. By changing the moment of freezing it was possible to separate the outlet pulse into two parts at different times. From the results of the analysis of the different parts of the pulse it was possible to restore the pattern of distribution of benzene and CH in the outlet pulse (points in Fig. 3),

The second method was based on the property of the additivity of the retention time (t) and the spreading (dispersion σ^2) of the substances. The times at which benzene, CH, and methane issued from the supplementary column and their spreading were determined by separate experiments. According to the literature [4],

$$t_{\rm s} = t_{\rm r} + t_{\rm c} \tag{1}$$

$$\sigma_{o}^{2} = \sigma_{o}^{2} + \sigma_{o}^{2} \tag{2}$$

The indices r, c, and s relate to the reactor, the column, and the reactor + column system, respectively. Under our conditions, the spreading of the pulses of benzene and CH in the capillary + column system scarcely differed from the spreading of the corresponding pulses in the capillary alone, although the spreading of the same pulses in the column, i.e., when the

TABLE 1

		Column 1 m long		Column 2 m long	
Hydrocarbon	v,* ml/min	$\sigma_{\rm C}^2$, min ²	^t c' ^{min}	$\sigma_{\rm c}^2$, min ²	t _c , min
Benzene Cyclohexane	1,65 0,80 1,65 0,80	0,405 2,055 0,151 0,577	6,0 12,9 2,05 4,25	0,577 2,540 0,190 0,722	11,8 24,1 4,1 8,3

*Rate of flow of carrier gas.

pulses fed from the metering device directly into the column, was considerable. This is probably connected with the fact that narrow pulses of hydrocarbons issuing from the metering device were more highly distorted in the columns than the wider pulses passing in from the reactor, since the latter had far smaller longitudinal concentration gradients causing the spreading of the pulses.

This hypothesis is confirmed by the fact that the splitting of the pulses of benzene and CH in the column used with a length of 1 m and in a similar column with a length of 2 m differed very slightly (Table 1). Consequently, the term σ_c^2 in Eq. (2) can be neglected. The validity of this is also confirmed by the fact that the forms of the total peak of benzene and CH recorded directly at the outlet from the reactor (see Fig. 3, curve 4) and that calculated as the sum of the outlet curves of benzene (curve 2) and of CH (curve 1) from the separating column after the deduction of t_c for each component and without taking spreading in the latter into account (curve 3) were extremely close. The two methods gave approximately the same results, but the second method (with the additional column) was less laborious and it was therefore used subsequently.

It can be seen from Fig. 3 that the maximum of the peak of the CH formed issued approximately simultaneously with the maximum of the peak of unchanged benzene, but by the time 95% of the unchanged benzene had issued only 75% of the CH formed had done so. Similar results were observed at rates of flow of the carrier gas of 0.85-1.3 ml/min.

In some experiments, CH was fed to the reactor together with the benzene, and its outlet peaks are denoted in Figs. 2 and 3 as $C_6H_{12}(1)$. This CH issued from the capillary earlier than the CH formed from the benzene, and its time of issuance coincided with the time of issuance under similar conditions in the absence of benzene [2]. For the α phase of the alloy-hydrogen system ($P_{H_2} = 1$ torr), this difference in the times of issuance amounted to 3-4 min. For the β phase of the alloy-hydrogen system ($P_{H_2} = 42-760$ torr), with the complete and partial hydrogenation of the benzene this difference amounted to ~50 sec in the interval of rates of flow of the carrier gas studied of 0.85-1.3 ml/min.

Some results showing the dependence of the conversion of the benzene and the amount of CH formed on P_{H_2} , the rate of flow of the carrier gas, and the amount of benzene fed in a pulse are given in Table 2 and in Fig. 4 (curve 2). It can be seen from these results that the conversion of the benzene and the amount of CH formed increased with a rise in P_{H_2} and with a decrease in the rate of flow of the carrier gas. With an increase in the amount of benzene fed in a pulse, the amount of CH formed increased, but the conversion of the benzene decreased.

Under the conditions of the existence of the α phase in our experiments an unusual result was obtained in comparison, for example, with those of Berman and Yanovskii [4], who investigated the cracking of cumene by a chromatographic method, the ratio of the adsorption capacity of the initial substance and the product being the same as in the reaction that we have studied; the product was adsorbed far more feebly than the initial substance. The weakly adsorbed reaction product (CH) issued from the catalyst capillary after the benzene. This can be explained only by a very slow hydrogenation of the adsorbed benzene molecule on the surface of the catalyst to CH, after which the CH molecule is desorbed. However, it is most probably the molecules of strongly absorbed benzene, and not the reversibly adsorbed form, that take part in such a conversion, as is confirmed by the zero order of the reaction. Furthermore, separate experiments on the treatment by hydrogen of a layer of strongly adsorbed benzene gave the same amount of CH as in the experiments on the hydrogenation of benzene on the α phase of the alloy-hydrogen system. With such a treatment of the catalyst, approximately 25% of the strongly adsorbed benzene was removed.



Fig. 4. Dependence of the conversion of a pulse of $1.07 \cdot 10^{-7}$ mole of benzene on $P_{\rm H_2}$ when hydrogen was fed through the wall of the capillary (1) and in a mixture with benzene vapor (2).

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Amount of C_6H_6 in a pulse, mole $\cdot 10^8$	₽ _{H₂} , torr	v*, m1/ min	Conversion, %	Amount of C_6H_{12} ob- tained, mole $\cdot 10^8$
4.8 4.8 4.8 4.8 9,6 9,6	70 30 70 30 70 30	1,2 1,2 0,9 0,9 0,9 0,9	75 51 91 65 78 42	3,60 2,45 4,42 3,12 7,48 4,03

*Rate of flow of carrier gas.

The peak of the CH formed in the reaction was comparatively narrow, although it should be considerably broadened under such conditions. In our previous work [2], a considerable increase in the absorption of CH on the alloy in the α phase in the presence of hydrogen was observed. If it is assumed that the adsorption of reactive hydrogen also increases in the presence of adsorbed CH, the rate of conversion of the strongly adsorbed benzene molecules will increase in the presence of CH. Then the CH desorbed at the beginning of the capillary, on moving through the capillary, will collect the CH formed in a narrow zone, accelerating the reaction in the following sections of the capillary.

In such a case, at small values of P_{H_2} (α phase), the catalytic centers participate in only one reaction act and the conversion time of the strongly adsorbed benzene into CH amounts to ~3-4 min (the difference in the times of issuance of the CH fed and that formed in the reaction). Benzene adsorbed on the β phase of the alloy-hydrogen system is converted into CH far more rapidly than on the α phase, since under these conditions the surface concentration of active hydrogen is far greater than on the α phase. In these circumstances, part of the weakly absorbed benzene probably also reacts with the hydrogen, up to the complete conversion of the 1.07·10⁻⁷ mole of benzene contained in the largest pulse, at P_{H_2} = 370 torr, although the possibility that under the conditions of existence of the β phase a rapid reaction of the strongly adsorbed benzene and that during the time of contact of the surface with benzene vapor on the passage of a pulse several acts of hydrogenation take place on each center strongly absorbing benzene cannot be excluded. The fact that the strongly adsorbed benzene takes part in the reaction is shown by the spreading of the CH peak as compared with the benzene peak in the region of large retention times.

The approximate coincidence of the times of issuance of the maxima of the benzene and CH peaks can be explained by the assumption that there is a mutual compensation of the influence of two factors. In the first place, the peak of the CH formed must outstrip the peak of the benzene, since benzene is more strongly adsorbed on the catalyst. In the second place, since the hydrogenation of benzene does not take place instantaneously, the CH formed should be desorbed later than the unconverted reversibly adsorbed benzene. The isotherm of the reversible adsorption of benzene on the α phase of the alloy ($P_{\rm H_2}$ = 1 torr) calculated from the outflow curves of the unchanged benzene in the presence of hydrogen are shown in Fig. 1 (curve 2). It can be seen from a comparison of curves 1 and 2 in Fig. 1 that hydrogen increases the adsorption of benzene. Under the conditions of existence of the β phase,

the adsorption of benzene at all values of P_{H_2} coincided with its adsorption on the alloy in the absence of H_2 .

The use as the adsorbent of a capillary made from the Pd-Ru alloy, which is permeable for hydrogen, permitted the adsorption of CH and benzene and the hydrogenation of benzene to be studied under the conditions of a feed of hydrogen to the surface of the catalyst by diffusion through the wall of the capillary [5].

In the course of these measurements, it was necessary to take into account the fact that with such a method of feeding hydrogen to the interior of the capillary the space velocity of flow of the gas within the capillary and P_{H_2} changed along the length of the capillary [6]. With a distribution of the partial pressure of the capillary along its length from zero to that measured at the outlet, the "outlet" pressure may also be connected with the formation of the α and β phases in the surface of the capillary. In experiments with variations in P_{H_2} at the external surface of the capillary from 70 to 760 torr, the outlet pressures ranged from 30 to 380 torr.

The absorption of CH and benzene under the conditions of the feeding of hydrogen by diffusion through the walls of the capillary was calculated from the chromatographic results [3, 7] taking the change in the rate of flow of the gases along the length of the capillary into account. As was found previously [2], in the range of existence of the α phase of the alloyhydrogen system, the adsorption of CH rose sharply. In experiments with the feed of hydrogen by diffusion through the wall of the capillary, even at small values of P_{H_2} at the outlet from the capillary (30 torr), when within it over a considerable part of its length P_{H_2} corresponded to the α phase, no sharp increase in the adsorption of CH was detected. It was likely that in these experiments the alloy was present as the β phase, which corresponds to the pressure of H_2 at the external wall of the capillary. This could take place if the permeability of alloy for hydrogen was determined by processes at the outlet surface for the hydrogen, as is generally observed in the low-temperature region.

The adsorption of the unchanged benzene under the conditions of the feeding of hydrogen by diffusion through the walls of the capillary also agreed with its absorption on the β phase of the alloy-hydrogen system. The degree of hydrogenation of the benzene depended on the method of feeding the hydrogen to the reaction zone. In Fig. 4, the dependences of the degrees of conversion of similar pulses of $1.0 \cdot 10^{-7}$ mole of benzene on P_{H_2} in the capillary when the hydrogen was fed into the capillary of the carrier gas and on the outlet value of P_{H_2} when the hydrogen was fed by diffusion through the wall of the capillary are compared. In spite of the small value of P_{H_2} within the capillary as compared with the outlet pressure, the feed of hydrogen by diffusion led to a greater rate of conversion of the benzene than the feed of gaseous H₂ within the capillary. This can be explained by assuming that when hydrogen is fed to the reaction zone through the wall of the capillary the surface concentration of its active (apparently, atomic) form exceeds the equilibrium concentration with respect to the partial pressure of gaseous H₂ in the capillary.

SUMMARY

1. The reversible adsorption of benzene vapor on an alloy of Pd with 6% of Ru at $303^{\circ}K$ under the conditions of existence of the α phase of the alloy-hydrogen system does not change, and in the region of existence of the β phase, it increases somewhat with a rise in the pressure of hydrogen. Strongly adsorbed benzene occupies $\sim7\%$ of the surface.

2. Only the strongly adsorbed benzene is hydrogenated on the α phase of the alloy-hydrogen system.

3. The feeding of hydrogen to the hydrogenation zone by diffusion through the alloy leads to a supersaturation of the surface with a form of chemisorbed hydrogen that is active in the benzene hydrogenation reaction.

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CHANGE IN THE DIFFERENTIAL MOLAR FREE ENERGY OF SORPTION OF A METHYLENE GROUP AS A FUNCTION OF THE LENGTH OF THE CHAIN OF AN n-ALKANE UNDER THE CONDITIONS OF GC ANALYSIS

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In GC, in agreement with a common idea [1], it is generally considered [2] that for a homologous series with a terminal functional group $C_nH_{2n+1}X$ the following relation is valid:

$$\Delta C_{RX} = \Delta G^X + (n-1) \Delta G^{CH_2} + \Delta G^{CH_3}$$
⁽¹⁾

where n is the number of C atoms; and ΔG^{X} , ΔG^{CH_2} , and ΔG^{CH_3} are, respectively, the contributions of the X, CH₂, and CH₃ groups to the total molar energy of sorption of the homolog (ΔG_{RX}). For n-alkanes Eq. (1) has the form

$$\Delta G_n = (n-2) \Delta G^{\text{CH}_2} + 2\Delta G^{\text{CH}_2}$$
⁽²⁾

Equation (2) presupposes the additivity of the contributions for a homologous series and, consequently, a linear dependence of ΔG_n on n. Additive methods of calculating retention parameters in GC are also based on the idea of the equivalence of the contributions of CH_2 and CH_3 groups in different compounds to them [3]. It is known [4] that ΔG_n can be calculated in GC from the retention parameters

$$\Delta G_n = -2.3RT \lg \frac{V_{gn}T\rho}{273} \tag{3}$$

where V_{gn} is the specific retention volume of an n-alkane with n carbon atoms; T is the temperature of analysis, °K; ρ = density of the stationary phase (SP) at the temperature of analysis; and R is the universal gas constant.

We have previously analyzed the dependence of log V_{gn} on the number of C atoms in nalkanes in the range of values of n of 2-18 on 10 stationary phases with different polarities [5]. It was found that on the SPs studied this dependence is nonlinear when a sequence of more than six homologs is considered. This permitted us to suggest the existence of a nonuniform change in the differential molar free energy of sorption in a series of n-alkanes (ΔG_n). Such a nonuniformity of the energy contributions with an increase in the length of the C chain should be shown, in the first place, in a difference in the contributions of a CH₂ unit as a function of the length of the chain.

In the present investigation, this hypothesis has been checked by calculating in a series of n-alkanes the change in the value of the differential molar free energy of sorption and also the energy contributions to it of each CH_2 unit in the homologs both under constant conditions of GC analysis and as functions of the temperature of analysis and the polarity of the SP.

DISCUSSION OF RESULTS

The analysis of the change in the value of the differential free energy and the energy contribution of CH_2 units to it in a series of n-alkanes was carried out in order to determine the influence of the polarity of the SP and the temperature of analysis. As a rule, the density (ρ) of an SP is unknown, but in calculating energies from formula (3) the contribution of the magnitude 2.3 RT log ρ to ΔG_n for homologs with $n \ge 3$ does not exceed 10% of the

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