JOURNAL OF CATALYSIS 22, 145–150 (1971)

Heats of Adsorption of Dialkylbenzenes on Silica-Alumina by Gas-Adsorption Chromatography

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Received February 4, 1970; revised October 23, 1970

Determinations have been made by a gas-chromatography method of the molar adsorption heats of 31 model dialkylbenzenes on a silica-alumina catalyst of the Houdry type. It has been demonstrated that there exists a dependence between the heats and the length, structure, and mutual position of the substituents in the benzene ring. A correlation has been found between the adsorption and the reactivity of the dialkylbenzenes on the silica-alumina catalyst.

INTRODUCTION

It has been established (*1–5*) in the course of catalytic conversions of model compounds of the dialkylbenzene series in the presence of a silica-alumina catalyst of the Houdry type that the following basic reactions take place: (a) dealkylation with subsequent removal of the side chains and formation of the corresponding monoalkylbenzene and benzene; (b) stepwise intramolecular isomerization involving a change in the mutual position of the substituents in the benzene ring; (c) fragmentation to dialkylbenzenes with a smaller number of carbon atoms in the side chains; (d) dehydrocyclization with the participation of one or both side chains as a result of which indane, tetralin, naphthalene, and anthracene structures are formed, and (e) disproportionation which is observed only in the case of diethylbenzenes. It became clear in the process of these investigations that the degree and character of the changes of the initial dialkylbenzenes are largely influenced by the length, structure, and mutual position of the substituents. The experimental results obtained were in agreement with thermodynamic calculations (*6*) made earlier about the reactions of dealkylation, isomerization, and disproportionation in the dialkylbenzene series.

With a view to a fuller interpretation of the structural effects observed, it has been interesting to determine the adsorption heats of different series of standard dialkylbenzenes under conditions close to those prevailing in the reactions. Such a possibility, as has been shown by M. Kraus and P. Strnad (*7*) and in an earlier work of ours in collaboration with I. Topalova and N. Petsev (*8*), is offered by the method of gas-adsorption chromatography.

In the present work this method has been applied in determining the adsorption heats of 31 individual dialkybenzenes.

EXPERIMENTAL

Apparatus. The retention volumes of the dialkylbenzenes investigated were determined by means of a Fractovap chromatograph, Model B, equipped with a high-temperature unit HI-750. The maximum working temperature of the apparatus, maintained with a precision of ±1°C, was 550°C. The chromatographic column was a U-shaped brass tube 28.5 cm long, i.d., 4 mm. The carrier gas used was high-purity nitrogen (99.999%). The flow rate of the carrier gas in all experiments was 20 ml/min.

Catalyst. The chromatographic column was filled with 1.87 g industrial-type silica-alumina Houdry catalyst, with particles

TABLE 1
Physical Constants of Dialkylbenzenes Investigated

Hydrocarbon	bp °C/mmHg	n_D^{20}	d_4^{20}	Ref.
1-Methyl-4-ethylbenzene	154/709	1.4964	0.8612	9
1,2-Diethylbenzene	177/706	1.5031	0.8823	10
1,3-Diethylbenzene	47/6	1.4951	0.8640	11
1,4-Diethylbenzene	83/29	1.4950	0.8620	9
1-Methyl-4-*n*-propylbenzene	175/705	1.4930	0.8560	9
1-Ethyl-4-*n*-propylbenzene	58/5	1.4967	0.8721	9
1,4-Di-*n*-propylbenzene	81/7	1.4914	0.8624	12
1,3-Di-*n*-propylbenzene	86/4	1.4923	0.8963	9
1-Methyl-4-*n*-butylbenzene	58/6	1.4900	0.8593	13
1-Methyl-3-*n*-butylbenzene	79/10	1.4917	0.8575	9
1-Methyl-2-*n*-butylbenzene	70/10	1.4950	0.8711	14
1,4-Diisopropylbenzene	—	1.4966	0.8602	Schuchardt
1,3-Diisopropylbenzene	—	1.4954	0.8567	Carlo Erba
1-Ethyl-4-*n*-butylbenzene	93/12	1.4990	0.8787	15
1-*n*-Propyl-4-*n*-butylbenzene	106–108/13	1.4920	0.8610	—
1,4-Di-*n*-butylbenzene	106–108/6	1.4915	0.8591	16
1,3-Di-*n*-butylbenzene	99–101/6	1.4935	0.8644	17
1,4-Di-sec-butylbenzene	88–89/4	1.4890	0.8598	14
1-Methyl-4-sec-butylbenzene	57/7	1.4900	0.8655	18
1-Ethyl-4-sec-butylbenzene	72/7	1.4920	0.8636	18
1-Iso-propyl-4-sec-butylbenzene	78/5	1.4892	0.8626	19
1-*n*-Propyl-4-sec-butylbenzene	77–79/5	1.4883	0.8633	—
1-Methyl-4-tert-butylbenzene	73.5–74.5/13	1.4953	0.8639	20
1-Ethyl-4-tert-butylbenzene	67–69/5	1.4942	0.8632	21
1-Isopropyl-4-tert-butylbenzene	95–97/10	1.4918	0.8606	22
1,4-Di-tert-butylbenzene	mp 75–77	—	—	9
1-Methyl-4-*n*-amylbenzene	101–103/18	1.4902	0.8544	14
1-Ethyl-4-*n*-amylbenzene	116–118/16	1.4913	0.8549	—
1-*n*-Propyl-4-*n*-amylbenzene	126–130/15	1.4900	0.8520	—
1-*n*-Butyl-4-*n*-amylbenzene	145/16	1.4892	0.8528	—
1,4-Di-*n*-amylbenzene	122/5	1.4968	0.8513	23

45–65 mesh in diameter. The composition of the catalyst was as follows: Al_2O_3, 10.65%, SiO_2, 86.91%, MgO, 0.7%, and oxides of iron, lead, and zinc, 1.74%. The specific surface area of the catalyst in the form of cylinders sized 4 × 4 mm, determined after the adsorption of benzene vapor at 20°C, was 235 m^2/g.

Hydrocarbons. Twenty-nine out of the total of 31 dialkylbenzenes investigated were synthesized by us mainly by the Würtz-Fittig method or by Clemmensen reduction of the respective ketones. The ketones were obtained by acylation of monoalkylbenzenes in the presence of anhydrous aluminium chloride at a temperature of about 0°C by the Friedel-Crafts method. The dialkylbenzenes were thoroughly purified by rectification in a column whose effectiveness was 36 theoretical plates. Their purity was checked chromatographically and by their infrared spectra. The physical constants and the literature sources used in the synthesis of the dialkylbenzenes are shown on Table 1.

Procedure. The catalyst was first heated for 2 hr at 550°C in flowing nitrogen, after which it was brought to the working temperature. Equal amounts of a given hydrocarbon were injected with a microliter injector of the Hamilton type. The retention volumes of the hydrocarbons on the catalyst did not depend on the sizes of the samples, which were different for the individual hydrocarbons, and were calculated by the formula (*24*):

$$V_R{}^m = \frac{t_R \cdot W_{fl} \cdot P_{fl} \cdot T}{m \cdot T_{fl} \cdot P_o} \cdot \frac{3}{2} \cdot \frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1}, \tag{1}$$

where:

t_R is corrected retention time;

W_{fl} is space velocity of the gas in the soap bubble flow meter;

P_{fl} is pressure of the gas in the flow meter;

T_{fl} is temperature of the gas in the flow meter;

T is temperature of the column;

P_i is pressure at the inlet of the column,

P_o is pressure at the outlet of the column; and

m is the amount of adsorbent in the column.

The molar adsorption heats were calculated using the formula:

$$Q = 2.303\, RS, \tag{2}$$

where R is the gas constant and S is the slope of the plot of $\log(V_R/T)$ vs $(1/T)$. It was found that within the temperature interval investigated this dependence was linear for all the dialkylbenzenes. By way of example, Figs. 1 and 2 show the plots for 1-*n*-butyl-4-*n*-amylbenzene and 1-isopropyl-4-tert-butylbenzene. The error of the adsorption heats was determined by the method of least squares and was found to be ±0.92 kcal/mole.

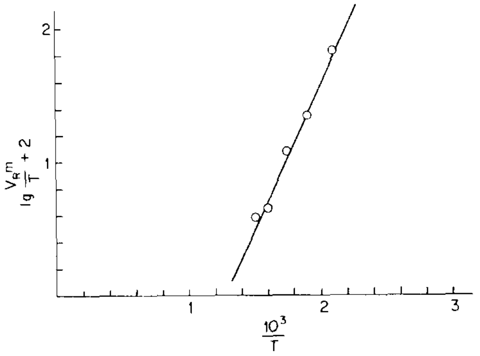

FIG. 1. The dependence $\log\left(\frac{V_R}{T}\right) = f\left(\frac{1}{T}\right)$ for 1-*n*-butyl-4-*n*-amylbenzene.

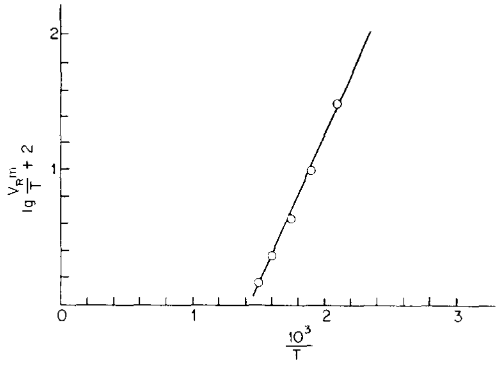

FIG. 2. The dependence $\log\left(\frac{V_R}{T}\right) = f\left(\frac{1}{T}\right)$ for 1-isopropyl-4-tert-butylbenzene.

RESULTS AND DISCUSSION

Table 2 shows the retention volumes related to 1 g of catalyst, together with the heats of adsorption. The data indicate that the heats vary from 5 to 10 kcal/mole. As with the monoalkylbenzenes (*8*), there is a general rise with increase in molecular weight. This is shown in Fig. 3, where the molar adsorption heats are plotted against the number of carbon atoms in the dialkylbenzenes. Figure 3 also shows that for a given molecular weight, the heats change appreciably with the structure and the mutual position of the two alkyl groups. For instance, with the C_{11} dialkylbenzenes these differences reach 3 kcal/mole.

The influence of the length of the normal side chains can be surveyed more fully in the following series: (a) 1,4-dimethylbenzene, 1-methyl-4-ethylbenzene, 1-methyl-4-*n*-propylbenzene, 1-methyl-4-*n*-butylbenzene, and 1-methyl-4-*n*-amylbenzene (Fig. 4a); (b) 1-methyl-4-*n*-butylbenzene, 1-ethyl-4-*n*-butylbenzene, 1-*n*-propyl-4-*n*-butylbenzene, 1,4-di-*n*-butylbenzene, and 1-*n*-amyl-4-*n*-butylbenzene (Fig. 4b); (c) 1-methyl-4-*n*-amylbenzene, 1-ethyl-4-*n*-amylbenzene, 1-*n*-propyl-4-*n*-amylbenzene, 1-*n*-butyl-4-*n*-amylbenzene, and 1,4-di-*n*-amylbenzene (Fig. 4c); (d) 1,4-dimethylbenzene, 1,4-diethylbenzene, 1,4-di-*n*-propylbenzene, 1,4-di-*n*-butylbenzene, and 1,4-di-*n*-amylbenzene (Fig. 4d).

The general principles underlying the influence of the molecular weight on the

TABLE 2

Retention Volumes and Adsorption Heats of Dialkylbenzenes on a Silica-Alumina Catalyst

Hydrocarbon	Retention volumes, ml/g Temp, °C 200	250	300	350	400	Adsorption heat in kcal/mole
1-Methyl-4-ethylbenzene	73.8	28.6	23.2	21.1	16.0	6.4
1,2-Diethylbenzene	83.6	34.8	25.1	30.7	21.6	6.7
1,3-Diethylbenzene	66.6	28.6	25.1	14.8	21.6	6.3
1,4-Diethylbenzene	70.6	31.2	20.4	20.0	21.6	5.5
1-Methyl-4-*n*-propylbenzene	72.2	30.4	27.9	33.8	20.4	5.3
1-Ethyl-4-*n*-propylbenzene	132.4	43.8	30.2	30.7	17.1	8.4
1,4-Di-*n*-propylbenzene	134.0	56.3	49.2	43.4	23.8	7.4
1,3-Di-*n*-propylbenzene	119.4	47.3	43.6	43.4	20.4	7.1
1-Methyl-2-*n*-butylbenzene	85.2	52.8	32.5	31.7	22.7	5.4
1-Methyl-3-*n*-butylbenzene	95.0	42.0	30.6	36.9	21.6	6.1
1-Methyl-4-*n*-butylbenzene	91.8	48.2	32.5	36.9	20.4	6.2
1,4-Di-isopropylbenzene	98.2	45.5	26.9	26.5	17.1	6.9
1,3-Di-isopropylbenzene	64.2	41.1	22.6	11.2	16.0	6.1
1-Ethyl-4-*n*-butylbenzene	124.2	68.0	46.4	36.9	21.6	6.9
1,4-Di-*n*-butylbenzene	250.8	104.5	39.1	36.9	21.6	9.2
1,3-Di-*n*-butylbenzene	177.8	72.4	44.9	13.8	19.3	8.9
1-*n*-Propyl-4-*n*-butylbenzene	140.4	69.7	56.6	42.4	21.6	7.4
1,4-Di-sec-butylbenzene	98.2	57.2	26.4	23.1	21.6	6.9
1-Methyl-4-sec-butylbenzene	61.0	36.7	16.6	15.9	13.7	6.3
1-Ethyl-4-sec-butylbenzene	86.8	44.7	27.4	22.1	12.6	7.5
1-Isopropyl-4-sec-butylbenzene	124.2	52.8	26.4	23.1	23.8	7.8
1-*n*-Propyl-4-sec-butylbenzene	133.2	51.0	26.4	32.1	19.3	8.1
1-Methyl-4-tert-butylbenzene	52.0	31.2	16.6	21.1	18.2	6.1
1-Ethyl-4-tert-butylbenzene	93.4	44.7	22.6	14.8	12.6	8.2
1-Isopropyl-4-tert-butylbenzene	150.2	55.4	25.4	14.8	9.8	10.0
1,4-Di-tert-butylbenzene	160.0	95.5	41.0	26.5	24.9	7.5[a]
1-Methyl-4-*n*-amylbenzene	111.2	58.1	28.3	28.6	26.3	6.4
1-Ethyl-4-*n*-amylbenzene	151.8	58.1	30.2	24.4	22.7	8.2
1-*n*-Propyl-4-*n*-amylbenzene	250.8	95.5	40.1	36.9	23.8	9.0
1-*n*-Butyl-4-*n*-amylbenzene	315.8	121.4	69.1	28.6	26.3	10.0
1,4-Di-*n*-amylbenzene	429.4	108.2	71.3	60.3	34.2	10.7

[a] In ether solution.

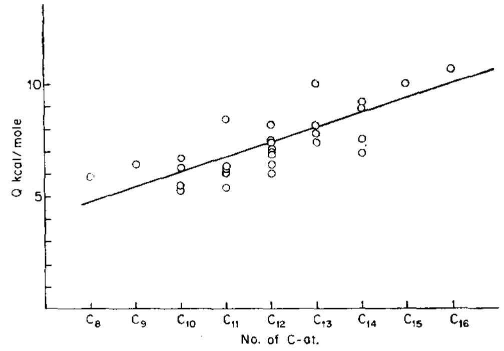

Fig. 3. The dependence of the adsorption heats on the number of carbon atoms in the molecules of the dialkylbenzenes.

values of the molar adsorption heats are also valid for the four series. Moreover, in series (b) and (c), the increase of the molecular weight by one methylene group has a considerably greater influence than in the (a) series. In the (d) series there is a relatively greater deviation from the linear character of this dependence at the transition from 1,4-dimethylbenzene to 1,4-diethylbenzene.

The dependence between structure and heat of adsorption is more complex. With the isomeric 1-methyl-4-butylbenzenes (1-methyl-4-*n*-butylbenzene-6,2; 1-methyl-4-sec-butylbenzene-6,3; and 1-methyl-4-tert-

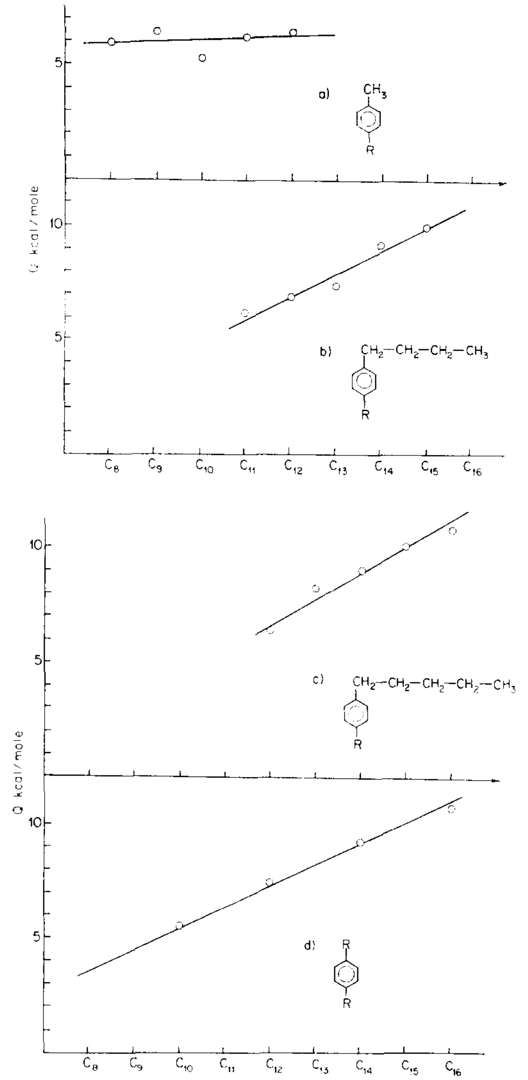

FIG. 4. a, b, c, d. Influence of the length of the normal side chains on the values of the molar adsorption heats. In all cases R=CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}.

butylbenzene-6,1) there are no essential differences in the molar adsorption heats depending on the structure of the side chain. In the isomeric 1-ethyl-4-butylbenzenes, there is a clearly expressed trend of a rise in the heats at the transition from normal to tertiary butyl group (1-ethyl-4-*n*-butylbenzene-6,9; 1-ethyl-4-sec-butylbenzene-7,5, and 1-ethyl-4-tert-butylbenzene-8,2). Such a trend is also apparent between 1-*n*-propyl-4-*n*-butylbenzene-7,4 and 1-*n*-propyl-4-sec-butyl-benzene-8,1. Utterly different in character is the dependence between the 1,4-di-*n*-butyl, 1,4-di-sec-butyl, and 1,4-di-tert-butylbenzenes in which the values of the adsorption heats change as follows: 9,2, 6,9 and 7,5.

There is no consistent influence of the mutual position of the substituents in the benzene ring on the adsorption heats. The differences are frequently within the limits of the errors of the method, and are sometimes of opposite sign. For instance, all paraisomers investigated by us, with the exception of *p*-diethylbenzene, show higher values of adsorption heats than the respective metaisomers. The opposite is observed with diethylbenzene; the metaisomer has higher values of molar adsorption heats than the paraisomer. Such a correlation between the meta and paraisomers has also been observed by Kraus and Strnad (*7*) in ethyltoluenes. Furthermore, our adsorption heat for 1-methyl-4-ethylbenzene (6,4) on silica-alumina agrees well with that found by Kraus and Strnad (6,2) for the same dialkylbenzene on alumina impregnated with aluminium fluoroborate.

The adsorption heats of the ortho-isomers in the case of xylenes and diethylbenzenes are higher than those for the para and metaisomers. In the case of the isomeric butyltoluenes, however, the ortho-isomer has the highest adsorption heat.

As already noted, the heats of adsorption increase linearly with molecular weight. The reactivity of the dialkylbenzenes, especially towards dealkylation, shows a similar dependence (*1–6*). The structure and the mutual position of the substituents in the benzene nucleus have a definite effect on the adsorption heats and on the character and degree of the catalytic conversions of the dialkylbenzenes over silica-alumina. It is difficult to make a strict correlation between the adsorption and the reactivity of the dialkylbenzenes, due to the complex character of the processes involved and to the limited number of standard hydrocarbons investigated. Nevertheless, the data obtained in this respect do testify to the explicit role of the adsorption in the catalytic conversions of dialkylbenzenes on silica-alumina.

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