

Statistical Molecular Calculation of Thermodynamic Parameters of Adsorption of Aromatic Hydrocarbons on Graphite

Part 2.—Polymethyl and Monoalkyl Benzenes

BY ANDREI V. KISELEV,[†] DIONIZAS P. POSHKUS* AND ARUNAS J. GRUMADAS

Institute of Chemistry and Chemical Technology of the Academy of Sciences of the Lithuanian S.S.R., Vilnius, U.S.S.R.

Received 18th July, 1977

A statistical molecular calculation is carried out of Henry's constant, K_1 , and of the differential change in internal energy, $\overline{\Delta U}_1$, for the adsorption of all the methyl and some monoalkyl derivatives of benzene on the basal plane of graphite at zero surface coverage. Thermodynamic parameters of adsorption of all the benzene derivatives investigated, calculated using the atom-atom approximation, are close to those obtained experimentally by adsorption chromatography on graphitized thermal carbon black. The basic reason for the difference between the thermodynamic parameters of adsorption of the structural isomers of polymethyl- and monoalkyl-derivatives of benzene on graphitized thermal carbon blacks lies in the differing geometric structure of their molecules.

As both we ¹ and Guiochon and co-workers ² showed previously, the thermodynamic parameters of adsorption at low (zero) surface coverage of the structural isomers of polymethylbenzenes on graphitized thermal carbon blacks (GTCB) are significantly different. These parameters vary particularly for polymethylbenzenes and their isomeric monoalkylbenzenes, and this difference increases with increasing numbers of carbon atoms in the molecules.¹ This is mainly due to two factors: first, the difference in geometric structure and secondly, the difference in electronic configuration in the molecules of the structural isomers of benzene derivatives. Differing views of the relative role of these two factors have been published.^{2, 3}

Statistical molecular calculations of the thermodynamic parameters of adsorption based on semi-empirical atom-atom potential functions of intermolecular interactions describe the difference between these parameters well for the structural isomers of the investigated saturated and non-saturated hydrocarbons on GTCB, these differences being determined by differences in the geometric structure of the isomers of these molecules.^{4, 5} In Part 1 ⁶ it was shown that the atom-atom approximation is also applicable to the case of intermolecular interactions of aromatic hydrocarbons with graphite. Therefore, statistical molecular calculations of the thermodynamic parameters of adsorption based on empirical atom-atom potential functions may be used to explain the basic reasons for the different intermolecular interactions of structural isomers of benzene derivatives with GTCB. Good agreement between the calculated and experimental values of K_1 would show that the basic reason is the different geometric structure of their molecules. However, a significant difference between the values calculated by the atom-atom approximation and the experimental values of K_1 for benzene derivatives would show that, together with differing in geometric structure, the difference in electronic configuration of the isomers is also significant in the case of structural isomers of these hydrocarbons. Molecular

[†] Institute of Physical Chemistry of the Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

statistical calculations were carried out by Guiochon and co-workers² for the thermodynamic parameters of adsorption of some methylbenzenes on the basal plane of graphite. However, in these calculations atom-atom potential functions used were evaluated only on the basis of the properties of adsorbate and adsorbent taken separately and without considering the influence of the electronic configuration of the carbon atoms on their intermolecular interaction. Such potential functions do not permit a good quantitative description of the thermodynamic parameters of adsorption of hydrocarbons on GTCB.

In this paper statistical molecular calculations of the thermodynamic parameters of adsorption are carried out for all methylbenzenes and some monoalkylbenzenes (ethyl-, isopropyl-, n-propyl- and n-butyl-benzenes) on the basal plane of graphite. In these calculations we have used atom-atom potential functions taking into account the influence of the electronic configuration of the C atoms in these hydrocarbons on their intermolecular interaction determined using experimental values of Henry's constant K_1 for the adsorption on GTCB of a few representatives of the classes of hydrocarbons under investigation.

THEORY

STATISTICAL MOLECULAR EQUATIONS

In the methylbenzenes internal rotation of the methyl groups is possible. Calculation of K_1 for the adsorption of methylbenzenes was carried out using the statistical equation⁵

$$K_1 = \frac{\int \dots \int \exp [-W(\alpha_1, \dots, \alpha_t)/kT] K_1(\alpha_1, \dots, \alpha_t) d\alpha_1 \dots d\alpha_t}{\int \dots \int \exp [-W(\alpha_1, \dots, \alpha_t)/kT] d\alpha_1 \dots d\alpha_t} \quad (1)$$

where $W(\alpha_1, \dots, \alpha_t)$ is the potential energy of internal rotation of the molecule, $\alpha_1, \dots, \alpha_t$ are the angles of internal rotation and $K_1(\alpha_1, \dots, \alpha_t)$ are the values of Henry's constant at fixed angles, $\alpha_1, \dots, \alpha_t$. The values of $K_1(\alpha_1, \dots, \alpha_t)$ were calculated from eqn (2)^{5, 6}

$$K_1(\alpha_1, \dots, \alpha_t) = \frac{1}{4\pi} \iint \left(\frac{2\pi kT}{\Phi_z''} \right)^{\frac{1}{2}} \exp \left(-\frac{\Phi_0}{kT} \right) \sin \theta d\theta d\psi \quad (2)$$

where Φ_0 and Φ_z'' are the potential energy of intermolecular interaction of a molecule of adsorbate with adsorbent and its second derivative with respect to z at equilibrium distance z_0 and fixed values of the angles $\alpha_1, \dots, \alpha_t$ and of the Euler angles θ and ψ .

In the case of free internal rotation of one or more groups in the molecule, W does not depend on the angles of internal rotation of these groups. In the case of free rotation of all the groups, $W = 0$ in eqn (1).

The calculations of K_1 for polymethylbenzenes having two or more CH_3 groups joined to adjacent C atoms in the benzene ring were also carried out with the use of models.⁷ These models take into account only the most energetically favourable orientations of the CH_3 groups in the isolated molecule. In this approximation

$$K_1 = \sum_{i=1}^m g_i K_{i,1} \quad (3)$$

where g_i is the normalised statistical weight of the i th model, $K_{i,1}$ is Henry's constant for this model and m is the number of models considered. Values of $K_{i,1}$ were calculated from eqn (2).

In monoalkylbenzenes internal rotation is possible both for the alkyl groups as a whole relative to the benzene ring (internal rotation around the $C_{\text{arom.}}-C$ bond) and around the $C-C$ bonds inside the alkyl group. The internal rotation around $C-C$ bonds in the alkyl groups is apparently close to that in alkanes, *i.e.* it is greatly hindered and gives rise to formation of rotational isomers in the case of *n*-propyl- and *n*-butyl-benzenes. In calculations of K_1 this rotation is taken into account using eqn (4):⁵

$$K_1 = \sum_{i=1}^m x_i^q K_{i,1} \quad (4)$$

where x_i^q is the mole fraction of the i th rotational isomer in the gas phase, $K_{i,1}$ is Henry's constant for this isomer and m is the number of possible rotational isomers.

In alkylbenzenes the ethyl and isopropyl groups were considered rigid with crossed positions of the $C-H$ bonds joined to the neighbouring C atoms. The internal rotation of the ethyl and isopropyl groups relative to the benzene ring was taken into account using eqn (1). The internal rotation of the *n*-propyl and *n*-butyl groups as a whole relative to the benzene ring and formation of rotational isomers due to internal rotation around the $C-C$ bonds in these groups was taken into account using eqn (5):

$$K_1 = \frac{\int \exp [-W(\alpha)/kT] \sum_{i=1}^m x_i^q K_{i,1}(\alpha) d\alpha}{\int \exp [-W(\alpha)/kT] d\alpha} \quad (5)$$

where $W(\alpha)$ is the potential function of internal rotation of the alkyl group relative to the benzene ring, α is the angle of this internal rotation and $K_{i,1}(\alpha)$ is Henry's constant for the i th rotational isomer at a fixed value of α .

Further, calculation of K_1 for isopropylbenzene was carried out as for an equilibrium mixture of rotational isomers which are formed by rotation around the $C_{\text{arom.}}-C$ bond, *i.e.* using eqn (4).

Calculations of the differential molar changes in internal energy, $\overline{\Delta U}_1$, of the adsorbate on adsorption were carried out using equations derived from eqn (1)-(5) of this paper and relation (2) of part 1.⁶ The values of differential molar changes of heat capacity, $\overline{\Delta C}_1$, for polymethyl and monoalkyl derivatives of benzene calculated using stated approximations of the internal rotation of these molecules showed large errors. Therefore they are not presented here.

CALCULATION OF POTENTIAL ENERGY Φ OF INTERMOLECULAR INTERACTION BETWEEN MOLECULE AND ADSORBENT

To find the intermolecular interaction between the C atoms of aromatic nucleus and the C atoms of graphite we used the atom-atom potential function obtained in part 1:⁶

$$\phi_{C(\text{benzene}) \dots C(\text{graphite})} = -1.48 \times 10^{-3} r^{-6} - 2.30 \times 10^{-5} r^{-8} + 2.03 \times 10^5 \exp (-35.7 r) \quad (6)$$

where ϕ is expressed in kJ mol^{-1} and r is the distance between the atoms in nm.

The electronic configurations of C and H atoms which are directly bound to C atoms of the aromatic nucleus differ from their electronic configuration in alkanes. However, in the present calculations these effects were neglected. To find the intermolecular interaction with the C atoms of graphite of all the C atoms of the

methyl and alkyl groups, of the H atoms attached to the C atoms of aromatic nucleus and of the H atoms attached to the C atoms of the methyl and alkyl groups, we used the atom-atom potential functions which we had obtained for the adsorption of alkanes on GTCB earlier:^{4, 5}

$$\phi_{\text{C(alkane)} \dots \text{C(graphite)}} = -1.386 \times 10^{-3} r^{-6} - 2.148 \times 10^{-5} r^{-8} + 1.89 \times 10^5 \exp(-35.7 r) \quad (7)$$

and

$$\phi_{\text{H} \dots \text{C(graphite)}} = -0.498 \times 10^{-3} r^{-6} - 0.950 \times 10^{-5} r^{-8} - 3.60 \times 10^4 \exp(-35.7 r). \quad (8)$$

The summation of ϕ over the C atoms of the graphite lattice was carried out as previously,^{4, 6} using Crowell's approximation. The lengths of the valence bonds in the molecules are shown in table 1. All valence angles were assumed normal, *i.e.* 109.5° for the sp^3 hybridisation of C atoms and 120° for the C atoms in the aromatic rings.

TABLE 1.—LENGTH OF VALENCE BONDS (nm)

molecule	bond					ref.
	C _{arom.} —C _{arom.}	C _{arom.} —C	C—C	C—H	C _{arom.} —H	
toluene	0.1392	0.152	—	0.111	0.1084	8
xylene	0.140	0.150	—	0.111	0.1084	8
trimethylbenzenes	0.140	0.150	—	0.109	0.1084	8
tetramethylbenzenes	0.140	0.150	—	0.109	0.109	
pentamethylbenzene	0.140	0.150	—	0.109	0.109	
hexamethylbenzene	0.1417	0.153	—	0.1125	—	9
ethylbenzene	0.1397	0.152	0.1536	0.1114	0.1084	8
n-propylbenzene	0.1397	0.152	0.154	0.108	0.1084	8
isopropylbenzene	0.1397	0.150	0.153	0.110	0.1083	10
n-butylbenzene	0.1396	0.1507	0.1535	0.110	0.1085	11

RESULTS AND DISCUSSION

METHYLBENZENES

The internal rotation of the methyl group in toluene is close to free rotation,^{7, 12, 13} as is that of methyl groups in polymethylbenzenes which do not have neighbours in *ortho* positions.¹²⁻¹⁵ At the same time the internal rotation of two methyl groups joined to adjacent carbon atoms in the benzene ring in 1,2-dimethylbenzene,^{7, 12-14} 1,2,4-trimethylbenzene⁷ and 1,2,4,5-tetramethylbenzene^{7, 14, 16} is greatly hindered (the potential barrier W_0 is ≈ 8 kJ mol⁻¹). Analogous potential barriers are also observed for the outermost methyl groups on increasing the number of neighbouring methyl groups: for the 1st and 3rd methyl groups in 1,2,3-trimethylbenzene^{14, 15} and 1,2,3,5-tetramethylbenzene¹⁵ and for the 1st and 4th methyl groups in 1,2,3,4-tetramethylbenzene.¹⁴ However, in these compounds the barrier to internal rotation of methyl groups which have neighbours in the *ortho* position on both sides is evidently lower than those for the outermost groups referred to above.^{14, 15}

The internal rotation of methyl groups in hexamethylbenzene is evidently frictional,^{7, 17} and the barrier to such rotation is small^{7, 17, 18} (1-2 kJ mol⁻¹ per

methyl group^{17, 18}). CH_3 groups in hexamethylbenzene vibrate with large amplitude perpendicular to the plane of the benzene ring;^{9, 17, 18} at 340 K the amplitude of this vibration is $\approx 9.9^\circ$.⁹ The potential minimum for internal rotation is found for the arrangement of the methyl groups shown in fig. 1.^{9, 17} This arrangement of CH_3 groups conforms to the established S_6 symmetry of the hexamethylbenzene molecule.^{7, 18} The benzene ring is not distorted in this molecule.⁷



FIG. 1.—Position of methyl groups in hexamethylbenzene molecule at potential minimum of internal rotation. The apices of triangles represent the positions of H atoms and the centres of triangles represent positions of C atoms of the methyl groups.

In calculating the thermodynamic parameters of adsorption of these hydrocarbons, the internal rotation of the methyl groups which do not have neighbours in the *ortho* position was considered to be completely free. For internal rotation of methyl groups which have one or two neighbouring methyl groups in the *ortho* position the following models were used:

MODEL 1. The internal rotation of the CH_3 groups is described by the potential function W , calculated by the semi-empirical method.¹⁹

MODEL 2. The internal rotation of the CH_3 groups is geared and is described by a pathway of lowest energy in the potential energy surface as calculated in ref. (7) and (16).

MODEL 3. The CH_3 groups have fixed orientations as in the models in ref. (7).

MODEL 4. The internal rotation of the CH_3 groups is completely free.

Calculations of K_1 for *o*-xylene were carried out using all four models; for 1,2,3-trimethylbenzene using models 1, 3 and 4; and for 1,2,4-trimethylbenzene using models 2 and 3. Since the values of K_1 for *o*-xylene, 1,2,3- and 1,2,4-trimethylbenzenes calculated using models 1, 2 and 3 were close, calculations of K_1 for the tetramethylbenzenes and pentamethylbenzene were performed using only the simplest model 3. Calculations of $\overline{\Delta U}_1$ for *o*-xylene were carried out using models 2 and 3 (the values of $\overline{\Delta U}_1$ obtained using these models were practically coincident) and for tri-, tetra- and penta-methylbenzenes using model 3 only.

Calculated and experimental^{1, 2} values of $\ln K_1$ and $\overline{\Delta U}_1$ for toluene and the isomeric xylenes are presented in fig. 2. The calculated values of $\ln K_1$ and $\overline{\Delta U}_1$ for toluene are in good agreement with the corresponding experimental values [to avoid duplication we indicate only some of the experimental K_1 values obtained in ref. (1) and (2)].

The calculated values of K_1 for *o*-xylene are only slightly dependent on the model taken for W . The calculated values of K_1 are lowered only insignificantly by neglecting the restricted rotation of the CH_3 groups. In fig. 2(a) the curves of $\ln K_1$ against $1/T$ for *o*-xylene calculated using different models for internal rotation fuse into one. The calculated values of K_1 for the xylene isomers are close to one another and to the experimental values.^{1, 2} The calculated values of K_1 for *m*-xylene are lower than those for *o*- and *p*-xylene in agreement with the experimental results.

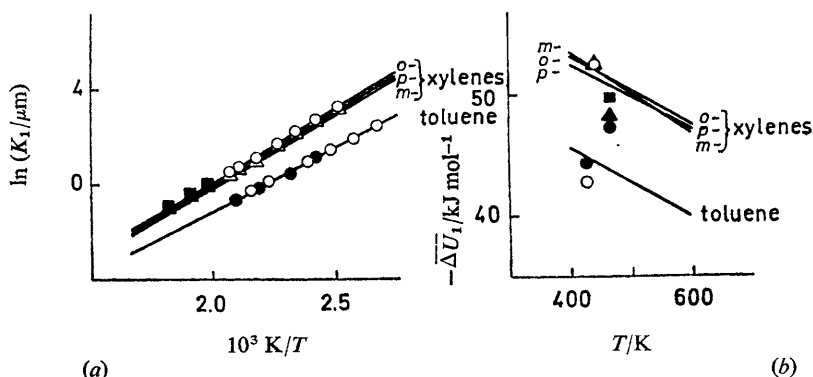


FIG. 2.—Calculated (curves) and experimental (dots) values of K_1 (a) and ΔU_1 (b) for adsorption on GTCB of toluene and *o*- (○, ●) *m*- (△, ▲) and *p*-xylenes (■). Open dots are taken from ref. (1) and filled dots from ref. (2).

However, the experimental values of K_1 for *o*- and *p*-xylene are close, while the calculated values for *o*-xylene are noticeably higher than those for *p*-xylene.

Calculation of the thermodynamic parameters of adsorption for methylbenzenes were performed in ref. (2) using three models (A, B and C) for the dependence of Φ on the position of the molecule on the surface. In model A it was assumed that movement of the centre of mass of the molecule along the surface and rotation around the axis perpendicular to the surface were free. In model B, in addition to the assumptions made in model A, it was assumed that vibrations of the centre of mass of the molecule perpendicular to the surface were harmonic. The approximations made in these two models result, however, in only small differences in the calculated values of K_1 .⁵ Approximations identical to those in model B² were made in our calculations. In model C² in addition to the assumptions made for models A and B, it was assumed that the librations of the adsorbed molecules around the axis parallel to the surface are harmonic. However, the latter approximation is crude: it significantly lowers the values of K_1 calculated for benzene.²⁰ K_1 values for the structural xylene isomers, calculated in ref. (2) using models A and B, are in the sequence $o > m > p$, while our calculated K_1 values for *m*- and *p*-xylenes are in the reverse sequence. This disagreement is caused by the fact that in ref. (2) the same values of z_0 and consequently of Φ_0 were used for all the structural xylene isomers, whereas in our calculations differences in the values of Φ_0 were taken into consideration for these isomers. The values of $-\Phi_0$, which we calculated for the isomeric xylenes at appropriate orientations of the CH_3 groups, decrease in the order $o > m > p$ and the difference in $-\Phi_0$ for *o*- and *p*-xylenes was 0.8–2.1 kJ mol⁻¹ (for different orientations of the CH_3 groups). The sequence of K_1 values, found in ref. (2) using model C, for the xylene isomers ($p > o > m$) is different from the sequence of the values of K_1 found using models A and B² and in our calculations. This is because, by changing the restricted rotation of the adsorbed molecules to their harmonic librations around the axis parallel to the surface, the calculated K_1 values for the structural isomeric xylenes are decreased differently: the values of K_1 for *o*- and *m*-xylenes decrease more than for *p*-xylene.

The divergence between the sequence of K_1 values for *o*- and *p*-xylenes which we calculated and the experimental values are caused by small differences in the electronic structure (polarisability) of these isomeric xylenes, which we have not taken into

consideration. The mean polarisability of *o*-xylene is $\approx 1\%$ less than those of *m*- and *p*-xylenes, which are approximately the same.²¹ Taking this electronic effect into account would lower by $\approx 1\%$ the potential function of interaction of *o*-xylene with the adsorbent (compared with the interaction of the other xylene isomers) as a consequence of which the calculated curve of $\ln K_1$ against $1/T$ for *o*-xylene would be shifted to the right along the $1/T$ axis by the same percentage, and would practically coincide with the calculated curve for *p*-xylene, in agreement with experiment.

The calculated values of $\overline{\Delta U}_1$ for the xylenes are also close to the experimental values [fig. 2(b)]. The sequence of calculated values of $-\overline{\Delta U}_1$ depends upon temperature: it changes from $m > o > p$ at 400 K (differing from the sequence of calculated K_1 values at 400 K) to $o > p > m$ at 600 K (coinciding with the sequence of calculated K_1 values at 600 K). The experimental values of $-\overline{\Delta U}_1$ determined in ref. (1) practically coincide for all xylenes, while the sequence of the experimental values of $-\overline{\Delta U}_1$ found in ref. (2) ($p > m > o$) differs from the sequence of calculated values. Such ambiguity in the sequences of calculated and experimental values of $\overline{\Delta U}_1$ is caused by errors in these values. $-\overline{\Delta U}_1$ values for the isomeric xylenes calculated in ref. (2) using models A and B follow the sequence $o > m > p$, corresponding to the sequence of K_1 values calculated for these models; but the $\overline{\Delta U}_1$ values, calculated using model C, are the same for all three isomers.

In fig. 3 are presented the calculated and experimental^{1, 2} values of $\ln K_1$ and $\overline{\Delta U}_1$ for various values of T for tri-, tetra- and penta-methylbenzenes. For all the structural isomers of tri- and tetra-methylbenzenes the calculated K_1 values are close to experimental^{1, 2} and follow the same sequence. The calculated values of K_1 for pentamethylbenzene coincide with the experimental values.¹ The sequence of the values of K_1 for the structural isomers of tri- and tetra-methylbenzenes calculated in ref. (2) are the same for all three models (A, B and C) used and coincide with the sequence of K_1 values which we calculated.

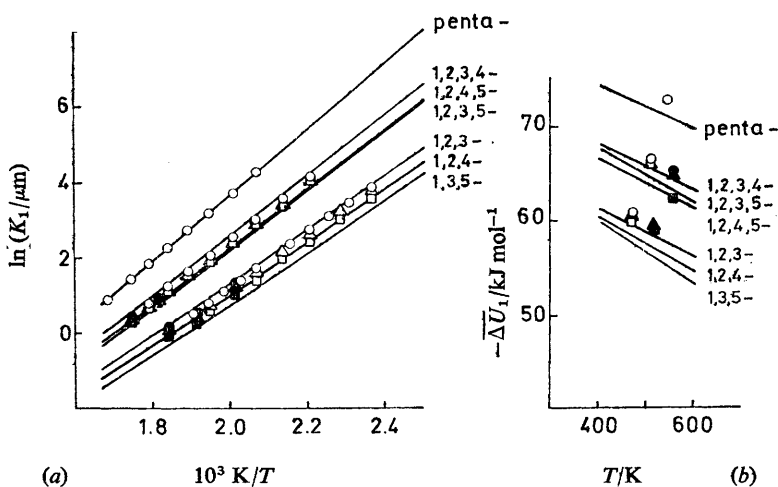


FIG. 3.—Calculated (curves) and experimental (dots) values of K_1 (a) and $\overline{\Delta U}_1$ (b) for adsorption on GTCB of trimethylbenzenes 1,2,3- (○, ●), 1,2,4- (△, ▲), 1,3,5- (□, ■); tetramethylbenzenes 1,2,3,4- (○, ●), 1,2,4,5- (△, ▲), 1,2,3,5- (□, ■) and pentamethylbenzene (○). Open dots are taken from ref. (1) and filled dots from ref. (2).

Our calculated values of $-\overline{\Delta U}_1$ for tri-, tetra- and penta-methylbenzenes are close to experimental.^{1, 2} The sequence of our calculated values of $-\overline{\Delta U}_1$ for the trimethylbenzenes (1,2,3 > 1,2,4 > 1,3,5) coincides with the sequence found experimentally in ref. (1) but differs from the sequence of experimental values of $-\overline{\Delta U}_1$ (1,2,4 > 1,2,3 = 1,3,5) found in ref. (2). Further, the sequence of our calculated values of $-\overline{\Delta U}_1$ for the tetramethylbenzenes (1,2,3,4 > 1,2,3,5 > 1,2,4,5) differs from the sequences of experimental values of $-\overline{\Delta U}_1$ found in ref. (1) (1,2,3,4 > 1,2,3,5 = 1,2,4,5) and ref. (2) (1,2,3,4 > 1,2,4,5 > 1,2,3,5). This discrepancy both between the experimental values of ref. (1) and (2) and the calculated and experimental values is caused by the uncertainty in these values. New, more accurate, experimental data are desirable here.

Calculation of the thermodynamic parameters of adsorption of hexamethylbenzene was performed for some structural models of the molecule. The internal rotation of the CH₃ groups was assumed to be geared. Three values of the potential barrier W_0 to this internal rotation were taken: $W_0 = 0, 2.1 \text{ kJ mol}^{-1}$ and ∞ . Further, two models were assumed for the geometric structure of the molecule: (1) the C—CH₃ bonds lie in the plane of the benzene ring; (2) the C—CH₃ bonds deviate to different sides alternately from the plane of the benzene ring by 9.9° .

The experimental K_1 and $\overline{\Delta U}_1$ values¹ and those calculated using these models are shown in fig. 4, which shows in the case of the planar structure of the molecule (dashed curves) that the calculated K_1 values depend only slightly on W_0 and lie above the experimental values. This is in accordance with the fact that the C atoms in the hexamethylbenzene molecule do not lie in one plane. When the deviation of the C—CH₃ bond from the plane of the benzene ring is taken into consideration (solid curves) the calculated values of K_1 depend strongly on W_0 . This is because, with the deviation of the methyl groups from the plane of the ring and with the

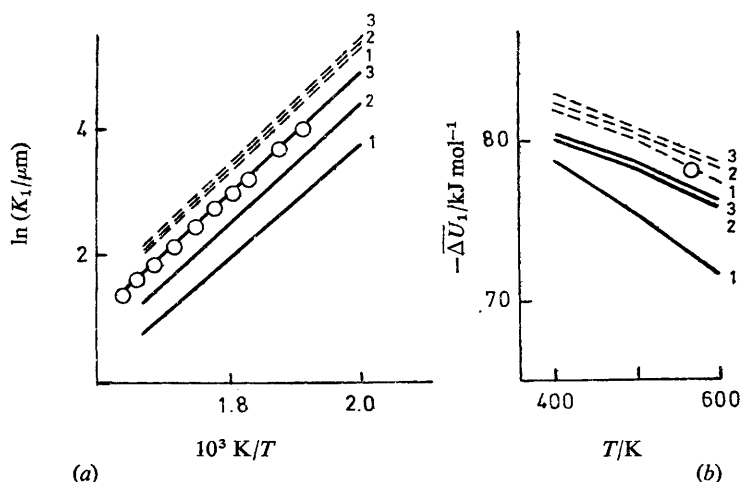


FIG. 4.—Calculated (curves) and experimental (dots) values of K_1 (a) and $\overline{\Delta U}_1$ (b) for adsorption on GTCB of hexamethylbenzene. The dashed lines are obtained on the assumption that all C atoms lie in one plane, the solid lines are obtained on the assumption that the C—CH₃ bonds deviate alternately to different sides of the plane of the benzene ring by 9.9° . The potential barrier W_0 for internal geared rotation of CH₃ groups was taken as 0 (curves 1), 2.1 kJ mol^{-1} for one CH₃ group (curves 2) and ∞ (curves 3).

parallel orientation of the flat benzene ring relative to the surface of the adsorbent, the molecule of hexamethylbenzene may be pushed from the surface by the atoms of hydrogen, leading to a significant increase in the equilibrium distance of the centre of mass of the molecule from the surface. In this case the orientation of the methyl groups has a strong influence on the equilibrium distance. The experimental K_1 values lie close to the continuous curve 3 obtained for a fixed orientation of CH_3 groups shown in fig. 1 ($W_0 = \infty$).

The experimental value of $-\Delta\bar{U}_1$ lies on the dashed line 1 calculated assuming that all C atoms lie in one plane, but it is also close to the continuous line 3 calculated on the assumption that the $\text{C}-\text{CH}_3$ bonds deviate from the plane of the benzene ring. More accurate measurements are also necessary here.

MONOALKYLBENZENES

Experimental and theoretical data for the potential function W of internal rotation of the alkyl group relative to the benzene ring are apparently only available for ethylbenzene²²⁻²⁵ and isopropylbenzene^{10, 24} at present. The internal rotation of the ethyl group relative to the benzene ring is hindered (the potential barrier is $>4 \text{ kJ mol}^{-1}$)^{22, 23, 25} and the potential minimum is found when the C atoms of the ethyl group are placed in the plane perpendicular to the plane of the benzene ring.²³ The internal rotation of the isopropyl group relative to the benzene ring is also hindered.¹⁰ However, in this case two potential minima are possible; one with the $\text{C}-\text{H}$ bond in the plane of the benzene ring and the other with the $\text{C}_\alpha-\text{C}_\beta$ bond located in this plane when the first minimum will be 3.3 kJ mol^{-1} lower than the second.^{10, 24}

We performed calculations of the thermodynamic parameters of adsorption of *n*-alkylbenzenes for the following models of internal rotation of the alkyl group relative to the benzene ring; (1) free internal rotation and (2) the potential function W of internal rotation of the *n*-alkyl group described by eqn (9)

$$W = (W_0/2)(1 - \cos 2\alpha) \quad (9)$$

where W_0 is the magnitude of the potential barrier and α is the angle of internal rotation. It was assumed that in all the *n*-alkylbenzenes examined the potential minimum is found with the $\text{C}_\alpha-\text{C}_\beta$ bond of the alkyl group located in the plane perpendicular to the plane of the benzene ring ($\alpha = 0$). For ethylbenzene, W_0 was taken as 5.4 kJ mol^{-1} .²² For the other *n*-alkylbenzenes for which the value of W_0 is not known exactly, W_0 was taken as 8.4 kJ mol^{-1} .

As noted previously, internal rotation around $\text{C}-\text{C}$ bonds in alkyl groups is evidently close to that in alkanes. In calculations of the molar fractions x_i^q of the rotational isomers of *n*-propyl- and *n*-butyl-benzenes, formed by internal rotation in the *n*-propyl- and *n*-butyl-groups, the difference in free energy ΔF for *gauche* and *trans* rotational isomers was evaluated using the expression $\Delta F_i = 2.5 g_i \text{ kJ mol}^{-1}$, where g_i is the number of *gauche* positions in the *i*th isomer of the molecule.⁵

We performed calculations of the thermodynamic characteristics of adsorption of isopropylbenzene (cumene) for the following models of internal rotation of the isopropyl group relative to the benzene ring; (1) free internal rotation, (2) the potential function of internal rotation W is given by eqn (10)²⁶

$$W = \frac{1}{6}[W_0 + 2W_1 + 2W_2 - (2W_0 - 2W_1 - 2W_2) \cos \alpha - (-2W_0 + 2W_1 + 2W_2) \cos 2\alpha - (W_0 + 2W_1 - 2W_2) \cos 3\alpha] \quad (10)$$

where in this expression $W_0 = 15.1$, $W_1 = 11.7$ and $W_2 = 3.3 \text{ kJ mol}^{-1}$. This

function has a minimum at $\alpha = 0$ (the $C_\alpha-H$ bond lies in the plane of the benzene ring) and two identical minima at $\alpha = 120$ and 240° , which are 3.3 kJ mol^{-1} higher than the first minimum. The potential barrier between adjacent minima is 11.7 kJ mol^{-1} . (3) Isopropylbenzene is a mixture of two conformational forms A and B (cf. fig. 5). In form A the $C_\alpha-H$ bond lies in the plane of the benzene ring and in form B the $C_\alpha-C_\beta$ bond lies in this plane. Values of 0 and 3.3 kJ mol^{-1} were taken for the differences between the free energies ΔF of these forms, form A being considered the most energetically favourable.

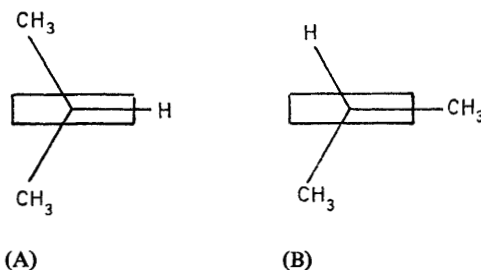


FIG. 5.—Conformational forms of isopropylbenzene.

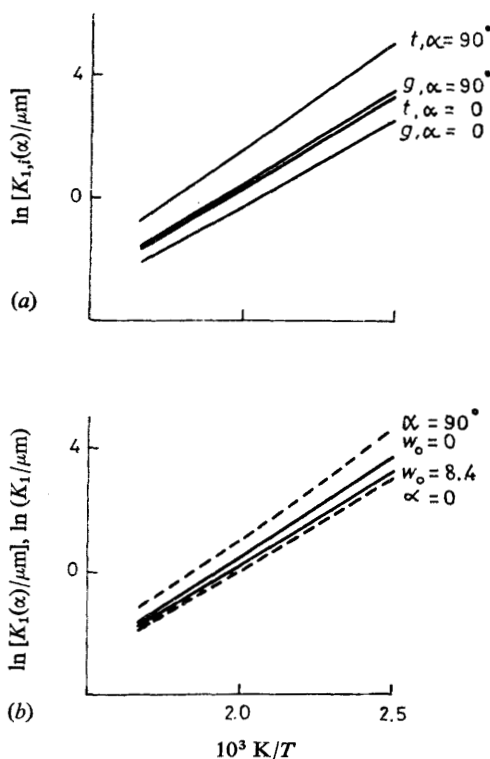


FIG. 6.—Calculated values of Henry's constant for adsorption of n-propylbenzene: (a) $K_{t,g}(\alpha)$ for *trans* (*t*) and *gauche* (*g*) rotational isomers at values of angle of internal rotation $\alpha = 0^\circ$ and 90° ; (b) $K_1(\alpha)$, statistically averaged over the rotational isomers at values of the angle $\alpha = 0^\circ$ and 90° (dashed curves) and K_1 , statistically averaged both over rotational isomers and also over angles α at values of $W_0 = 0$ and 8.4 kJ mol^{-1} (solid curves).

In fig. 6(a) are shown the calculated values of $K_{1,i}(\alpha)$ for *trans* (*t*) and *gauche* (*g*) rotational isomers of n-propylbenzene for two fixed values of the angle α of internal rotation of the propyl group relative to the benzene ring: $\alpha = 90^\circ$ (atoms C_α and C_β lie in the plane of the ring) and $\alpha = 0^\circ$ (atoms C_α and C_β lie in the perpendicular plane). The $K_{1,i}(\alpha)$ values are strongly dependent on the orientation of the n-propyl group relative to the benzene ring, *i.e.* on the angle α and on the form (*t* or *g*) of the rotational isomer of the propyl group.

In fig. 6(b) are shown $K_1(\alpha)$ values for n-propylbenzene at two values of angle α (dashed curves) calculated using eqn (4), *i.e.* statistically averaged over the rotational isomers, and K_1 values for n-propylbenzene calculated using eqn (5) (solid curves), *i.e.* statistically averaged both over rotational isomers and over α , at two values of the potential barrier to internal rotation of the propyl group relative to the benzene ring, $W_0 = 0$ and 8.4 kJ mol^{-1} . The K_1 values statistically averaged over the rotational isomers are strongly dependent on α . K_1 values statistically averaged over the rotational isomers and angles α depend on W_0 but this dependence is comparatively weak (values of K_1 at $W_0 = \infty$ coincide with values of $K_1(\alpha)$ at $\alpha = 0^\circ$). Analogous results were also obtained for the other alkylbenzenes which we examined.

In fig. 7 are shown K_1 and $\overline{\Delta U}_1$ values for ethyl-, n-propyl-, isopropyl- and n-butyl-benzenes calculated assuming free rotation (solid curves) and restricted rotation of the alkyl group relative to the benzene ring (dashed curves). The obtained values of K_1 and $\overline{\Delta U}_1$ for isopropylbenzene, which has been considered as a mixture of

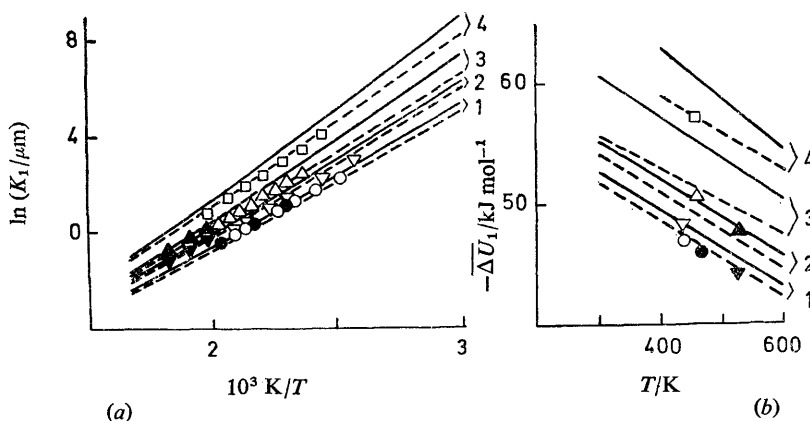


FIG. 7.—Calculated (curves) and experimental (dots) values of K_1 (a) and $\overline{\Delta U}_1$ (b) for adsorption on GTCB of alkylbenzenes: ethyl- (curves 1; \circ , \bullet), isopropyl- (curves 2; ∇ , \blacktriangledown), n-propyl- (curves 3; \triangle , \blacktriangle) and n-butyl-benzene (curves 4; \square). The solid curves are obtained at $W_0 = 0$, the dashed curves at $W_0 = 5.4 \text{ kJ mol}^{-1}$ for ethylbenzene, $W_0 = 8.4 \text{ kJ mol}^{-1}$ for n-propyl- and n-butyl-benzenes and $\Delta F = 3.3 \text{ kJ mol}^{-1}$ for isopropylbenzene. The open dots are taken from ref. (1) and filled dots from ref. (27).

rotational isomers with $\Delta F = 0$ and 3.3 kJ mol^{-1} , practically coincide with the respective values obtained assuming free and restricted rotation of the propyl group. The corresponding experimental values obtained on GTCB^{1, 27} are also shown in fig. 7. The experimental values of K_1 and $\overline{\Delta U}_1$ for all alkylbenzenes studied are close to the dashed curves calculated for the model of restricted rotation of the alkyl group in accordance with the restricted internal rotation of the alkyl group relative to the benzene ring. The calculated values of K_1 for isopropylbenzene are lower than those for n-propylbenzene, in agreement with experiment.

COMPARISON OF POLYMETHYL- AND MONOALKYL-BENZENES

In fig. 8 calculated and experimental values of K_1 and $\overline{\Delta U}_1$ at 473 K are compared for mono-n-alkylbenzenes and the corresponding polymethylbenzenes in which all the methyl groups are joined to adjacent C atoms in the benzene ring. For hexamethylbenzene the values of K_1 and $\overline{\Delta U}_1$ obtained for $\beta = 9.9^\circ$ and $W_0 = \infty$ are presented. For mono-n-alkylbenzenes K_1 and $\overline{\Delta U}_1$ values calculated for $W_0 = 8.4 \text{ kJ mol}^{-1}$ are given. Experimental values of K_1 at 473 K were obtained by interpolation or extrapolation of the values found in ref. (1) and (27). Moreover we neglected the dependence of the experimental $\overline{\Delta U}_1$ values^{1, 2, 27} on temperature. As is evident from fig. 8, the calculated values satisfactorily describe the differences in the experimental values of K_1 and $\overline{\Delta U}_1$ for the polymethylbenzenes and their isomeric monoalkylbenzenes.

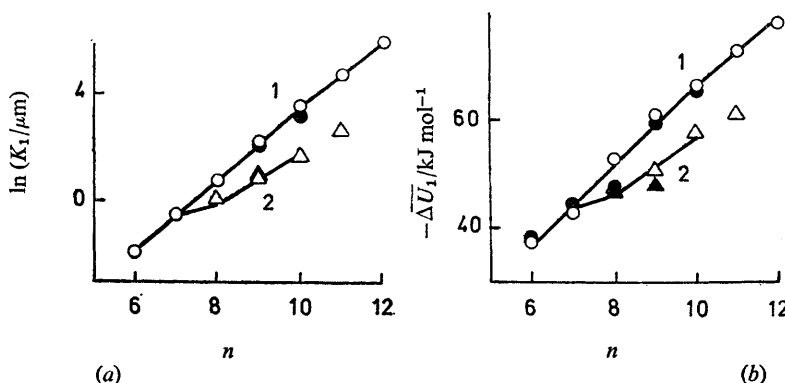


FIG. 8.—Calculated (curves) and experimental (dots) values of K_1 (a) and $\overline{\Delta U}_1$ (b) for polymethylbenzenes with CH_3 groups joined to adjacent C atoms in benzene ring (curves 1; ○, ●) and mono-n-alkylbenzenes at $W_0 = 8.4 \text{ kJ mol}^{-1}$ (curves 2; Δ, ▲) at 473 K as a function of the number n of carbon atoms in a molecule. The open dots are taken from ref. (1) and filled dots from ref. (2) and (27).

Thus the main reason for the differences in thermodynamic parameters of adsorption of the structural isomers of polymethyl- and monoalkyl-derivatives of benzene on GTCB lies in their differing geometric structure. Differences in their electronic structures contribute little to the variation in these parameters. The thermodynamic parameters of adsorption on GTCB of polymethyl and monoalkyl derivatives of benzene, as of aromatic hydrocarbons with condensed nuclei, may be calculated in good agreement with experimental values on the basis of the structure of their molecules and semi-empirical atom-atom potential functions taking into account the influence of the electronic configuration of the C atoms on their intermolecular interactions.

The authors thank G. Guiochon, E. V. Kalashnikova and K. D. Shcherbakova for communication of new experimental data on adsorption of alkylbenzenes and G. Curthoys for his interest and for translating the paper into English.

¹ E. V. Kalashnikova, A. V. Kiselev, R. S. Petrova, D. P. Poshkus and K. D. Shcherbakova, *Chromatographia*, in press.

² C. Vidal-Madjar, M.-F. Gonnord and G. Guiochon, *J. Colloid Interface Sci.*, 1975, **52**, 102

- ³ H.-J. Hofmann, W. Engewald, D. Heidrich, J. Porschmann, K. Thieroff and P. Uhlmann, *J. Chromatogr.*, 1975, **115**, 299.
- ⁴ A. V. Kiselev and D. P. Poshkus, *J.C.S. Faraday II*, 1976, **72**, 950.
- ⁵ N. N. Avgul, A. V. Kiselev and D. P. Poshkus, *Adsorbciya Gasov i Parov na Odnorodnikh Poverkhnostyakh* (Adsorption of Gases and Vapours on Homogeneous Surfaces) (Khimiya, Moscow, 1975).
- ⁶ A. V. Kiselev, D. P. Poshkus and A. J. Grumadas, *J.C.S. Faraday I*, 1979, **75**, 1281.
- ⁷ W. R. Woolfenden and D. M. Grant, *J. Amer. Chem. Soc.*, 1966, **88**, 1496.
- ⁸ *Spravochnik khimika* (Chemist's Handbook) (Goskhimizdat, Moscow, 1963), vol. 1.
- ⁹ R. R. Karl, Y. C. Wang and S. H. Bauer, *J. Mol. Struct.*, 1975, **25**, 17.
- ¹⁰ L. V. Vil'kov, N. I. Sadova and S. S. Mochalov, *Doklady Akad. Nauk S.S.S.R.*, 1968, **179**, 896.
- ¹¹ V. G. Dashevsky, *Zhur. strukt. Khim.*, 1970, **11**, 489.
- ¹² K. S. Pitzer, *Disc. Faraday Soc.*, 1951, **10**, 66.
- ¹³ C. A. Wulf, *J. Chem. Phys.*, 1963, **39**, 1227.
- ¹⁴ J. J. Rush, *J. Chem. Phys.*, 1967, **47**, 3936.
- ¹⁵ T. D. Alger, D. M. Grant and R. K. Haris, *J. Phys. Chem.*, 1972, **76**, 281.
- ¹⁶ K. V. Mirskaya and L. V. Ivanova, *Kristallographia*, 1973, **18**, 168.
- ¹⁷ W. C. Hamilton, J. W. Edmonds, A. Tippe and J. J. Rush, *Disc. Faraday Soc.*, 1969, **48**, 192.
- ¹⁸ J. E. Overberger, W. A. Steele and J. G. Aston, *J. Chem. Thermodynamics*, 1969, **1**, 535.
- ¹⁹ A. I. Kitaigorodsky and V. G. Dashevsky, *Tetrahedron*, 1968, **24**, 5917.
- ²⁰ A. V. Kiselev and D. P. Poshkus, *Doklady Akad. Nauk S.S.S.R.*, 1961, **139**, 1145; *Trans. Faraday Soc.*, 1963, **59**, 428; *Zhur. fiz. Khim.*, 1963, **37**, 608.
- ²¹ J. Homer and M. C. Cooke, *J. Chem. Soc. (A)*, 1969, 1984.
- ²² F. G. Brickwedde, M. Moskow and R. B. Scott, *J. Chem. Phys.*, 1945, **13**, 547.
- ²³ J. Križ and J. Jakeš, *J. Mol. Struct.*, 1972, **12**, 367.
- ²⁴ J. Štokr, H. Pivcova, B. Schneider and S. Dirlikov, *J. Mol. Struct.*, 1972, **12**, 45.
- ²⁵ A. Miller and D. W. Scott, *J. Chem. Phys.*, 1978, **63**, 1317.
- ²⁶ M. V. Volkenshtein, *Doklady Akad. Nauk S.S.S.R.*, 1945, **49**, 111.
- ²⁷ G. Guiochon and C. Vidal-Madjar, personal communication.

(PAPER 8/1753)