

Equilibria of isomeric transformations and relations between thermodynamic properties of secondary alkylbenzenes

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Equilibria of mutual transformations of monoamylbenzenes and diamylbenzenes (AMB), monohexylbenzenes (HXB), monoheptylbenzenes (HPB), and monodecylbenzenes (DB) have been studied in the liquid state over the range 273 to 423 K in the presence of 3 to 9 mass per cent of AlCl_3 . Values of $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ for the reactions studied have been calculated from the temperature dependences of the equilibrium constants. Below are given the reactions and the corresponding values for $\Delta_r H_m^\circ/(\text{kJ}\cdot\text{mol}^{-1})$ and $\Delta_r S_m^\circ/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$: 3-AMB = 2-AMB, $-(0.16 \pm 0.08)$, (8.45 ± 0.23) ; 3-HXB = 2-HXB, $-(0.30 \pm 0.07)$, (3.85 ± 0.21) ; 3-HPB = 2-HPB, $-(0.21 \pm 0.07)$, (3.52 ± 0.22) ; 3-DB = 2-DB, $-(0.23 \pm 0.14)$, (3.51 ± 0.43) ; 4-HPB = 3-HPB, (0.02 ± 0.41) , (7.57 ± 1.29) ; 4-DB = 3-DB, (0.09 ± 0.41) , (1.69 ± 1.28) ; 5-DB = 4-DB, $-(0.01 \pm 0.09)$, (0.18 ± 0.25) . For *para-to-meta* transformations of diamylbenzenes the average molar reaction enthalpy is $-(0.26 \pm 0.46)$ $\text{kJ}\cdot\text{mol}^{-1}$ and the intrinsic change of molar entropy is $-(0.99 \pm 1.2)$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. It is shown that for the calculation of enthalpies of formation of secondary alkylbenzenes correlations can be used which do not take into account the position of the phenyl substituent on the aliphatic hydrocarbon chain. The calculation of enthalpies of formation of normal and secondary alkylbenzenes in the liquid state at 298.15 K is made on the basis of experimental and literature values.

1. Introduction

Hydrocarbons have been thoroughly studied. Their characteristics are taken as basic in making various additivity schemes to evaluate the properties of functional derivatives of organic compounds. However, even the best additivity schemes do not permit one to make dependable evaluations of the thermodynamic properties of isomers of most organic compounds. This situation can be explained by the lack of refined information about the contributions of groups, atoms, or bonds which is due to the absence of the necessary number of dependable values for properties of the basic compounds. In particular, such a situation exists in the series of alkylaromatic hydrocarbons for which rather detailed additivity schemes are valid only for primary alkylbenzenes^(1,2) and for some lower secondary alkylbenzenes (*sec-AB*).^(3,4) Turning to higher secondary alkylbenzenes, corrections that would allow for isomers differing in the position of the aromatic nucleus on the aliphatic carbon chain are not available for any single correlation.

Yet differences in the thermodynamic properties of isomers of *sec-AB* should

probably exist because of differences in their physical properties. This is also supported by paraffin hydrocarbons that differ only by the position of the methyl or alkyl group in a carbon chain having different physical and thermodynamic properties.^(2,5) Additivity schemes with varying degrees of refinement have been devised to allow for changes in thermodynamic properties brought about by changes in structure. To obtain precise values for the enthalpies of formation and entropies of secondary alkylbenzenes, we have studied isomeric transformations of monoamylbenzenes and diamylbenzenes (AMB), monohexylbenzenes (HXB), monoheptylbenzenes (HPB), and monodecylbenzenes (DB).

2. Experimental

Alkylbenzenes were derived from the reaction of acetophenone, propiophenone, butyrophenone, and valerophenone with the corresponding alkyl-magnesium halogenides⁽⁶⁾ followed by hydrogenation of the alcohols formed in glacial acetic acid in the presence of palladium on charcoal.⁽⁷⁾

Diamylbenzenes were synthesized from *p*-dibromobenzene and *m*-dibromobenzene and the corresponding ketones by mixing them with magnesium in anhydrous ether. Alcohols thus formed were hydrogenated to diamylbenzenes using the methods described above.⁽⁷⁾ The compositions of all mono- and di-alkylbenzenes were substantiated by i.r. (UR-20) and n.m.r. (Bruker WP-80) spectra. The chromatographic purities of the preparations were not less than 99.0 mass per cent. Analysis of the reaction mixtures was made by g.l.c. with the help of a Chrom-4 apparatus with a flame-ionization detector and a glass capillary column (50.0 m long, 0.00025 m in diameter) with an immobile liquid phase (PEG-40 M). The column temperature was varied from 383 to 453 K at the rate of $0.07 \text{ K} \cdot \text{s}^{-1}$ during the amylbenzene analysis and was kept constant during the analysis of hexyl- (383 K), heptyl- (403 K), and decyl-benzene (433 K). All components of the equilibrium mixtures were completely separated and identified.

The various equilibria were studied in the interval 273 to 423 K in the liquid phase at atmospheric pressure in the presence of 3 to 9 mass per cent of AlCl_3 in the form of a catalytic complex. In calculating the total amounts of benzene and mono- and di-amylbenzene, the amount of side products in the investigation of the mutual transformation of amylbenzenes did not exceed 9 moles per cent at 423 K and 3 moles per cent at 293 K. In studying the isomerization of hexyl-, heptyl-, and decyl-benzenes the amounts of side products did not exceed 3 to 4 moles per cent (calculating the sum of benzene and monoalkylbenzenes) under the most difficult conditions of the experiment. The temperature was held and recorded with a precision of $\pm 0.1 \text{ K}$.

Experimental results show that for all reactions studied the values of K do not change with broad changes in the compositions of the reaction mixtures (within the limits of the errors in the definition). Therefore it is reasonable to suggest that the activity coefficients of the components of an equilibrium mixture are close to one another under the conditions of the experiment and that constants calculated from the mole fractions of components are true thermodynamic values.

The establishment of equilibrium was verified by the constancy of the values for K against change of the composition of the original mixture, time of reaction, and quantity of catalyst. The approach to the investigation of the equilibrium of mutual transformations of *sec*-AB is shown (as an example) for the isomerization of *sec*-monoamylbenzenes at 293 K (table 1). Analogous experiments were performed for all reactions studied and temperatures.

3. Results

Final results obtained in the investigation of the isomerization equilibria of secondary alkylbenzenes are given in table 2. Shown are the reactions studied, temperature T , the time τ of reaction, the number M of compositionally different starting mixtures taken for investigation, the number N of runs differing from one another either by the initial mixture, the catalyst, or the reaction time, the mean values $\langle K \rangle$ of the equilibrium constants, and their standard deviations. The number N was taken as a weight in calculating $\langle K \rangle$, because the deviation of equilibrium constants from the mean value was uniform in most cases.

Thermodynamic characteristics of the reactions, calculated from the temperature dependence of the equilibrium constants by the method of least squares, are shown in table 3. There too are shown intrinsic changes of reaction entropies calculated from the equation:

$$\Delta_r S_m^\circ(\text{intrinsic}) = \Delta_r S_m^\circ(\text{actual}) + R \ln(\sigma_2/\sigma_1) - R \ln(n_2/n_1), \quad (1)$$

where σ is the symmetry number of a molecule and n is the number of optical isomers of a molecule of starting substance (1) or reaction product (2).

The symmetry numbers of molecules shown in table 3 do not include those of methyl rotors. It is to be noted that in $\Delta_r S_m^\circ(\text{intrinsic})$ shown in table 3, correlations are not made for the entropy of mixing of rotating conformers, because there are no

TABLE 1. Results of investigations of reaction equilibrium: 3-AMB = 2-AMB at $T = 293$ K: mass fraction w of AlCl_3 , reaction time τ , and number N of runs

| Initial mixture | $10^2 w$ | t/h | N | K |
|---|----------|-----------|-------------|--------------------|
| 50 mass per cent of benzene 50 mass per cent of 3-AMB | 7 | 1.5 to 12 | 8 | 2.946 ± 0.02^a |
| 18 mass per cent of benzene 82 mass per cent of 2-AMB | 8 | 7 to 19 | 12 | 2.945 ± 0.033 |
| 6 mass per cent of benzene 47 mass per cent of 3-AMB 47 mass per cent of 2-AMB | 8 | 22 to 32 | 11 | 2.953 ± 0.018 |
| 50 mass per cent of benzene 50 mass per cent of 1,3-di(3-AM) _B ^b | 7 | 2 to 5 | 13 | 2.941 ± 0.015 |
| | | | Mean value: | 2.946 ± 0.012 |

^a Uncertainty is the standard deviation of the mean.

^b 1,3-di(3-amyl)benzene.

TABLE 2. Results of equilibrium investigations

| T/K | τ/h^a | M ^b | N ^c | $\langle K \rangle$ | M | N | $\langle K \rangle$ |
|---|------------|----------------|----------------|-------------------------------------|---|----|---------------------|
| 3-Am = 2-AnB | | | | 1-(2-Am), 4-(3-Am)B = 1,4-di(2-Am)B | | | |
| 293 | 1.5 to 32 | 4 | 44 | 2.946 ± 0.012 ^d | 4 | 47 | 1.491 ± 0.019 |
| 333 | 3 to 19 | 3 | 21 | 2.931 ± 0.012 | 3 | 32 | 1.439 ± 0.009 |
| 373 | 0.5 to 8 | 4 | 28 | 2.906 ± 0.010 | 4 | 30 | 1.408 ± 0.010 |
| 423 | 2 to 10 | 3 | 29 | 2.889 ± 0.011 | 3 | 31 | 1.399 ± 0.016 |
| 1-(2-Am), 3-(3-Am)B = 1,3-di(2-Am)B | | | | 1,4-di(3-Am)B = 1,3-di(3-Am)B | | | |
| 293 | 1 to 32 | 4 | 45 | 1.472 ± 0.005 | 3 | 38 | 1.965 ± 0.023 |
| 333 | 1 to 19 | 3 | 32 | 1.436 ± 0.012 | 3 | 29 | 1.964 ± 0.013 |
| 373 | 0.5 to 8 | 4 | 30 | 1.404 ± 0.005 | 3 | 25 | 1.891 ± 0.033 |
| 423 | 1 to 10 | 3 | 30 | 1.411 ± 0.006 | 3 | 27 | 1.919 ± 0.030 |
| 1-(2-Am), 4-(3-Am)B = 1-(2-Am), 3-(3-Am)B | | | | 1,4-di(2-Am)B = 1,3-di(2-Am)B | | | |
| 293 | 1 to 32 | 4 | 49 | 1.969 ± 0.010 | 3 | 35 | 1.957 ± 0.009 |
| 333 | 2 to 19 | 3 | 28 | 2.009 ± 0.008 | 3 | 28 | 1.993 ± 0.011 |
| 373 | 0.5 to 8 | 4 | 35 | 1.911 ± 0.019 | 4 | 35 | 1.907 ± 0.013 |
| 423 | 1 to 10 | 3 | 30 | 1.892 ± 0.088 | 3 | 28 | 1.955 ± 0.037 |
| 3-HXB = 2-HXB | | | | | | | |
| 273 | 1 to 16 | 3 | 25 | 1.815 ± 0.008 | | | |
| 303 | 0.5 to 11 | 2 | 17 | 1.797 ± 0.003 | | | |
| 333 | 1 to 20 | 2 | 22 | 1.756 ± 0.008 | | | |
| 373 | 0.5 to 5.5 | 2 | 20 | 1.757 ± 0.006 | | | |
| 403 | 0.5 to 4 | 2 | 15 | 1.741 ± 0.004 | | | |
| 3-HPB = 2-HPB | | | | 4-HPB = 3-HPB | | | |
| 273 | 0.5 to 16 | 3 | 30 | 1.676 ± 0.005 | 3 | 30 | 2.457 ± 0.013 |
| 303 | 0.5 to 11 | 2 | 19 | 1.662 ± 0.006 | 2 | 20 | 2.490 ± 0.011 |
| 333 | 1 to 20 | 2 | 23 | 1.660 ± 0.017 | 2 | 21 | 2.447 ± 0.010 |
| 373 | 0.5 to 5.5 | 2 | 20 | 1.638 ± 0.009 | 2 | 20 | 2.515 ± 0.015 |
| 403 | 0.5 to 4 | 2 | 15 | 1.624 ± 0.004 | 2 | 15 | 2.431 ± 0.019 |
| 3-DB = 2-DB | | | | 4-DB = 3-DB | | | |
| 273 | 0.5 to 16 | 3 | 30 | 1.681 ± 0.008 | 3 | 30 | 1.170 ± 0.005 |
| 303 | 0.5 to 11 | 2 | 19 | 1.665 ± 0.030 | 2 | 21 | 1.205 ± 0.005 |
| 333 | 1 to 20 | 2 | 23 | 1.674 ± 0.014 | 2 | 23 | 1.169 ± 0.006 |
| 373 | 0.5 to 5.5 | 2 | 20 | 1.618 ± 0.006 | 2 | 20 | 1.190 ± 0.005 |
| 403 | 0.5 to 4 | 2 | 15 | 1.618 ± 0.006 | 2 | 15 | 1.194 ± 0.004 |
| 5-DB = 4-DB | | | | | | | |
| 273 | 0.5 to 16 | 3 | 30 | 1.006 ± 0.009 | | | |
| 303 | 0.5 to 11 | 2 | 20 | 1.026 ± 0.003 | | | |
| 333 | 1 to 20 | 2 | 23 | 1.026 ± 0.003 | | | |
| 373 | 0.5 to 5.5 | 2 | 20 | 1.028 ± 0.003 | | | |
| 403 | 0.5 to 4 | 2 | 15 | 1.017 ± 0.002 | | | |

^a Reaction time.^b M is the number of compositionally different initial mixtures taken for investigation.^c N is the number of separate runs differing from one another either by a starting mixture, the catalyst, or the reaction time.^d Uncertainty is the standard deviation of the mean (for all entries in this table).

TABLE 3. Thermodynamic characteristics of studied reactions

| Reaction | $\langle T \rangle$ | $\Delta_r H_m^\circ(\langle T \rangle)$ | $\frac{n_2}{n_1}$ | $\frac{\sigma_2}{\sigma_1}$ | $\Delta_r S_m^\circ(\langle T \rangle)$ | $\Delta_r S_m^\circ(\text{intrinsic}, \langle T \rangle)$ |
|---|---------------------|---|-------------------|-----------------------------|--|---|
| | K | $\text{kJ} \cdot \text{mol}^{-1}$ | | | $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ | $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ |
| 1 3-amylybenzene = 2-amylybenzene | 341.9 | -0.16 ± 0.08^b | 2 | 1 | 8.45 ± 0.23^b | 2.69 ± 0.23^b |
| 2 1-(2-Am), 4-(3-Am)benzene = 1,4-di(2-Am)benzene | 368.2 | -0.42 ± 0.28 | 2 | 2 | 1.76 ± 0.75 | 1.76 ± 0.75 |
| 3 1-(2-Am), 3-(3-Am)benzene = 1,3-di(2-Am)benzene | 343.5 | -0.38 ± 0.41 | 2 | 1 | 1.89 ± 1.19 | 1.89 ± 1.19 |
| 4 3-hexylbenzene = 2-hexylbenzene | 325.0 | -0.30 ± 0.07 | 1 | 1 | 3.85 ± 0.21 | 3.85 ± 0.21 |
| 5 3-heptylbenzene = 2-heptylbenzene | 319.2 | -0.21 ± 0.07 | 1 | 1 | 3.52 ± 0.22 | 3.52 ± 0.22 |
| 6 3-decylbenzene = 2-decylbenzene | 314.2 | -0.23 ± 0.14 | 1 | 1 | 3.51 ± 0.43 | 3.51 ± 0.43 |
| 3-alkylbenzene = 2-alkylbenzene | 319.5 | -0.25 ± 0.13 | | | | 3.63 ± 0.38 |
| 7 4-heptylbenzene = 3-heptylbenzene | 321.4 | 0.02 ± 0.41 | 2 | 1 | 7.57 ± 1.29 | 1.81 ± 1.29 |
| 8 4-decylbenzene = 3-decylbenzene | 322.4 | 0.09 ± 0.41 | 1 | 1 | 1.69 ± 1.28 | 1.69 ± 1.28 |
| 4-alkylbenzene = 3-alkylbenzene | 321.9 | 0 ± 0.46 | | | | 1.75 ± 1.29 |
| 9 5-decylbenzene = 4-decylbenzene | 341.9 | -0.01 ± 0.09 | 1 | 1 | 0.18 ± 0.25 | 0.18 ± 0.25 |
| 5-alkylbenzene = 4-alkylbenzene | 341.9 | 0 ± 0.10 | | | | 0 ± 0.43 |
| 10 1,4-di(3-Am)benzene = 1,3-di(3-Am)benzene | 342.3 | -0.25 ± 0.27 | 1 | 0.5 | 4.77 ± 0.80 | -0.99 ± 0.80 |
| 11 1-(2-Am), 4-(3-Am)benzene = 1-(2-Am), 3-(3-Am)benzene | 326.5 | -0.30 ± 0.26 | 1 | 0.5 | 4.68 ± 0.80 | -1.08 ± 0.80 |
| 12 1,4-di(2-Am)benzene = 1,3-di(2-Am)benzene | 335.8 | -0.23 ± 1.12 | 1 | 0.5 | 4.85 ± 3.36 | -0.91 ± 3.36 |
| 1,4-disecalkylbenzene = 1,3-disecalkylbenzene | 334.9 | -0.26 ± 0.46 | | | | -0.99 ± 1.2 |

^a Calculation of the $\Delta_r S_m^\circ(\text{intrinsic}, \langle T \rangle)$ is described in the text.

^b The uncertainties include errors in the definition of $\langle K \rangle$ and the errors of $\langle K \rangle$'s dispersion depending on the linear dependence in the coordinates $\{\log_{10}(\langle K \rangle) - K/T\}$ for different temperatures and correspond to the uncertainty intervals.

literature data on conformers' composition of *sec*-AB. The errors in the thermodynamic properties have been calculated in accordance with the requirements of the IUPAC Commission using methods stated in reference 8.

4. Discussion

Reactions studied by us, together with their thermodynamic properties, have been grouped in table 3 according to the type of transformation. The table also shows average values of enthalpy and entropy changes for each type. Derived average values have been defined with enough precision to be used as the basis for the calculation of thermodynamic functions of secondary alkylbenzenes. As the average temperature of the investigations is close to 298.15 K, the properties of the reactions studied can be assumed to refer to the standard temperature.

Table 3 shows that practically all isomeric transformations are accompanied by small enthalpy effects. However, if reactions of the type $4\text{-AB} = 3\text{-AB}$ and $5\text{-AB} = 4\text{-AB}$ have changes of enthalpy equal to zero, then for transformations of the type $3\text{-AB} = 2\text{-AB}$, $\Delta_r H_m^\circ$ differs from zero by more than the limits of the error of measurements, e.g. $-(0.25 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$. Enthalpies of the isomeric

transformation of 3-, 4-, and 5-phenylalkanes, practically equal to zero, permit us to conclude that $\Delta_f H_m^\circ$ at 298.15 K of liquid isomers of *sec*-AB, beginning from 3-AB and proceeding towards the centre of the aliphatic chain, have equal values. Thus, a correction taking into account the position of the aromatic nucleus in an aliphatic chain should quite reasonably be accepted in any of the additivity schemes for all *sec*-AB compounds (excluding 2-AB). Comparison with methylalkanes for which the analogous difference is (2.5 ± 1.2) kJ·mol⁻¹ (calculated by us on the basis of $\Delta_f H_m^\circ$ values for liquid methylalkanes given in reference 9), shows that in terms of enthalpies of formation *sec*-AB compounds differ less than aliphatic hydrocarbons with similar structures.

On the basis of the above conclusions we have calculated and recommend for practical calculations values of coefficients applicable to a correlation scheme similar to that of Good:⁽³⁾

$$\Delta_f H_m^\circ(\textit{sec}\text{-AB}, l, 298.15 \text{ K}) = \Delta_f H_m^\circ(\text{C}_6\text{H}_6, l, 298.15 \text{ K}) + \sum a_i n_i, \quad (1)$$

where a_1 is a contribution for the replacement of H attached to an aromatic ring by a CH₃-CH-CH₃ group; a_2 is a contribution for the insertion of a CH₂ group in an alkyl chain; a_3 is a contribution for the replacement of H attached to an aromatic ring by a CH₃ group, and n_i is the number of substitutions of a type. The correlation in equation (1) can be used for the calculation of enthalpies of formation of liquid normal and *sec*-AB as well as of *meta*- and *para*-disec-AB. The calculation of $\Delta_f H_m^\circ(l, 298.15 \text{ K})$ of *ortho*-substituted alkylbenzenes requires inclusion in the present scheme of such members as allow for the $\Delta_f H_m^\circ$ contribution from the mutual influence of two alkyl substituents in their *ortho*-positions. The value $a_1 = -(90.17 \pm 1.22)$ kJ·mol⁻¹ has been found on the basis of $\Delta_f H_m^\circ$ at 298.15 K of liquid isopropylbenzene, $-(41.13 \pm 1.09)$ kJ·mol⁻¹; and benzene, (49.04 ± 0.54) kJ·mol⁻¹ taken from reference 9. On the basis of the molar enthalpies of formation of liquid isopropylbenzene and *sec*-butylbenzene, normal propyl- and butylbenzenes, as well as nine linear alkanes (from butane to dodecane) taken from reference 9, an average weighted value $a_2 = -(25.43 \pm 0.66)$ kJ·mol⁻¹ has been derived. Almost equal corrections for the CH₂ fragment for secondary, $-(25.3 \pm 1.7)$ kJ·mol⁻¹, and primary, $-(25.5 \pm 1.5)$ kJ·mol⁻¹, alkylbenzenes and aliphatic hydrocarbons, $-(25.43 \pm 0.79)$ kJ·mol⁻¹, have been calculated and a mean value of a_2 has been taken for the processing of enthalpies of formation.

The value $a_3 = -(36.86 \pm 0.69)$ kJ·mol⁻¹ is calculated from $\Delta_f H_m^\circ(\text{C}_6\text{H}_6, l, 298.15 \text{ K})$ and $\Delta_f H_m^\circ(\text{C}_6\text{H}_5\text{CH}_3, l, 298.15 \text{ K}) = (12.18 \pm 0.42)$ kJ·mol⁻¹ also derived from reference 9.

We have shown that the contribution to $\Delta_f H_m^\circ(\textit{sec}\text{-AB}, l, 298.15 \text{ K})$ of the interaction of two secondary-alkyl substituents attached to the *meta* position of the aromatic nucleus is equal to zero within the uncertainty limits, in contrast to the value for *meta*-interaction of alkyl groups equal to $-(0.76 \pm 0.15)$ kJ·mol⁻¹ found by Good⁽³⁾ on the basis of the energies of combustion of methyl-, ethyl-, and isopropyl-benzenes. This quantity, defined on the basis of reactions (10) to (12) (table 3) agrees well with the results of investigations of the isomerization of di-isopropylbenzenes.^(10, 11) Thus, the correction for *meta*-interaction of alkyl groups

found by Good does not have a universal character and cannot be recommended for the calculation of $\Delta_f H_m^\circ$ of liquid *sec*-alkylbenzenes with higher molar masses.

Noting that the calculated values of a_1 and a_2 have errors surpassing the enthalpy of transformation for $3\text{-AB} = 2\text{-AB}$, $-(0.25 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}$, refined contributions allowing for the substitution of the phenyl group in positions 2, 3, 4, *etc.*, of an aliphatic chain have to be neglected at the present time. However, with the accumulation of experimental values for $\Delta_f H_m^\circ(\text{sec-AB, l, 298.15 K})$ and diminishing errors in a_1 and a_2 , the introduction of the above refinement will be possible in calculating enthalpies of formation of *sec*-AB compounds of greater molar mass.

On the basis of the derived values for a_1 , a_2 , a_3 , and $\Delta_f H_m^\circ(\text{C}_6\text{H}_6, \text{l, 298.15 K})$ we calculated $\Delta_f H_m^\circ(\text{l, 298.15 K})$ of some normal- and *sec*-AB compounds as shown in table 4. There also are given experimental values of enthalpies of formation of liquid normal- and *sec*-AB compounds which can be found in the literature. The calculated values of enthalpies of formation of normal- and *sec*-AB are consistent with the experimental results within the limits of the errors of the experiment, with the exception of 3-phenylhexane. The experimental value for $\Delta_f H_m^\circ(3\text{-phenylhexane, l, 298.15 K})$ was calculated by Stull, Westrum, and Sinke⁽¹²⁾ on the basis of the enthalpy of combustion given in reference 13. However, the original article does not contain the starting experimental material needed for the evaluation of the validity of enthalpies of combustion. This did not permit us to explain the differences in $\Delta_f H_m^\circ(3\text{-phenylhexane, l, 298.15 K})$ predicted by us and shown in the work by Stull, Westrum, and Sinke.

The analysis of $\Delta_r S_m^\circ$ of isomeric transformations of *sec*-AB compounds shows that, as is so for $\Delta_r H_m^\circ$, intrinsic changes of entropies of reaction of each type have very similar values. The exception concerns the $3\text{-AB} = 2\text{-AB}$ type of transformation for which there is a difference in $\Delta_r S_m^\circ(\text{intrinsic})$ between amylbenzenes and multi-molecular AB compounds. For amylbenzenes, $\Delta_r S_m^\circ(\text{intrinsic})$ has a lower value compared with that for reactions of the type mentioned for other *sec*-AB compounds

TABLE 4. Standard molar enthalpies of formation of normal and secondary alkylbenzenes in the liquid state at 298.15 K

| Alkyl | Formula | $-\Delta_f H_m^\circ(n\text{-AB, l, 298.15 K})$ | | $-\Delta_f H_m^\circ(\text{sec-AB, l, 298.15 K})$ | |
|-------------|------------------------------|---|-------------------------|---|------------------------|
| | | $\text{kJ} \cdot \text{mol}^{-1}$ | | $\text{kJ} \cdot \text{mol}^{-1}$ | |
| | | this work | literature | this work | literature |
| ethyl- | C_6H_{10} | 13.3 ± 1.1^a | $12.34 \pm 0.79^{(9)}$ | | |
| propyl- | C_9H_{12} | 38.7 ± 1.3 | $38.33 \pm 0.79^{(9)}$ | 41.1 ± 1.3 | $41.13 \pm 1.09^{(9)}$ |
| butyl- | $\text{C}_{10}\text{H}_{14}$ | 64.1 ± 1.4 | $63.85 \pm 1.26^{(9)}$ | 66.6 ± 1.5 | $66.40 \pm 1.26^{(9)}$ |
| amyl- | $\text{C}_{11}\text{H}_{16}$ | 89.5 ± 1.6 | | 92.0 ± 1.6 | |
| hexyl- | $\text{C}_{12}\text{H}_{18}$ | 115.0 ± 1.7 | | 117.4 ± 1.8 | $141.4^{(12)}$ |
| heptyl- | $\text{C}_{13}\text{H}_{20}$ | 140.4 ± 1.8 | | 142.9 ± 1.9 | |
| octyl- | $\text{C}_{14}\text{H}_{22}$ | 165.8 ± 2.0 | | 168.3 ± 2.0 | |
| nonyl- | $\text{C}_{15}\text{H}_{24}$ | 191.3 ± 2.1 | | 193.7 ± 2.1 | |
| decyl- | $\text{C}_{16}\text{H}_{26}$ | 216.7 ± 2.2 | $217.86 \pm 2.09^{(9)}$ | 219.1 ± 2.2 | |
| eicosyl- | $\text{C}_{26}\text{H}_{46}$ | 471.0 ± 3.0 | | 473.4 ± 3.0 | $476.1 \pm 6.7^{(9)}$ |
| heneicosyl- | $\text{C}_{27}\text{H}_{48}$ | 496.4 ± 3.1 | | 498.9 ± 3.1 | $505.4 \pm 6.3^{(9)}$ |

^a The uncertainties correspond to the uncertainty intervals.

shown in table 3 for reactions (1), (4), (5), and (6). This is also shown by the equilibrium constant which is more sensitive than $\Delta_r S_m^\circ$ (intrinsic), and which over the whole range of temperature studied is substantially different for amylbenzenes and other alkylbenzenes (table 2). This anomaly is also observed in a series of aliphatic hydrocarbons. Dashevski⁽¹⁴⁾ noted the so-called "pentane effect", showing itself in some combinations of *trans* and *gauche* conformations in *n*-pentane being forbidden and the number of conformers in a molecule appearing to be less than expected. Dashevski noted also that such effects do not take place in hexane, heptane, and higher-molar-mass hydrocarbons. Thus, repetition of practically the same value of $\Delta_r S_m^\circ$ (intrinsic) for 3-hexylbenzene = 2-hexylbenzene, 3-heptylbenzene = 2-heptylbenzene, and 3-decylbenzene = 2-decylbenzene transformations should be considered typical for the whole *sec*-AB series with the exception of the first representative, amylbenzene. The analogous conclusion can also be made for transformations of the type 4-AB = 3-AB and 5-AB = 4-AB. For each of the given types of reaction we have found the average values of $\Delta_r S_m^\circ$ (intrinsic) which can be transferred to the whole series of *sec*-alkylbenzenes. Deviation of $\Delta_r S_m^\circ$ (intrinsic) from zero for 4-AB = 3-AB and 3-AB = 2-AB transformations can be explained by differences in number and mole fraction of conformers of 2-, 3-, and 4-*sec*-alkylbenzenes. A similar conclusion was arrived at in reference 15. Isomers such as 4- and 5-AB are probably characterized by practically equal values of $\Delta_{\text{mix}} S_m^\circ$ of conformers. The above discussion leads to an important conclusion. If the calculation of $\Delta_f H_m^\circ$ of liquid *sec*-AB at 298.15 K does not demand great refinement to allow for isomerization due to the position of an aromatic nucleus on an aliphatic chain, then in calculating entropies of *sec*-AB compounds the analogous approach will lead to major mistakes. In formulating additive schemes for the calculation of S_m° of *sec*-AB compounds it is necessary to include members which take into account the differences in entropies of mixing of conformers for isomers such as 3- and 2-alkylbenzene.

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