Pyrolysis of Di-*l*-isobornyl *d*-Camphorate.—Di-*l*-isobornyl *d*-camphorate, 37.7 g., was heated for 5 hours at 235–260°, whereby 11.7 g. of distillate containing water and a dark semi-solid residue, 23.2 g., were obtained.

After separating the water, the distillate was refractionated over sodium. The main fraction, 7.5 g., was a solid, boiling at 157–159° and melting at 40°. It was made liquid with a few drops of benzene and oxidized with 1250 ml. of an aqueous solution containing 26 g. of potassium permanganate and 3 g. of potassium hydroxide by efficient stirring for 24 hours at room temperature. The solution was then decolorized with sodium bisulfite and steam distilled. The ether extract of the steam distillate yielded a minute residue with a strong camphor odor, but the quantity was too small to permit the identification of tricyclene. The residue from the steam distillation was filtered free from manganese dioxide, evaporated to about 50 ml. in a stream of nitrogen, acidified with dilute sulfuric acid, extracted with ether and the ether layer evaporated after drying with anhydrous sodium sulfate. The residue, 5.3 g., was treated with acetyl chloride in the same manner as described above for the separation of *d*-camphoric acid from *l*-isocamphoric acid, since camphenic acid does not form an anhydride.

Four grams of camphenic acid was obtained. It was recrystallized from water, m.p. 135.5–136.5° (uncor.); calcd. for $C_{10}H_{16}O_2$, neut. equiv., 200.23; found neut. equiv., 200.62, 199.48. It did not lower the melting point of an authentic sample in the mixed melting point test. This result establishes the presence of camphene.

The ether solution from the acetyl chloride treatment yielded no residue upon evaporation, showing the absence of camphoric anhydride, hence of bornylene.

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Thermodynamic Functions of Adsorbed Molecules from Surface Tension Measurements: Toluene, Benzene and *n*-Heptane on Mercury[1]

BY TERRELL L. HILL AND CHARLES KEMBALL

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Methods of calculating thermodynamic functions of adsorbed molecules from adsorption isotherm measurements[2] or calorimetric measurements[3,4] have been discussed recently. In order to obtain the molar internal energy $\mathrm{E_S}$ and entropy $\mathrm{S_S}$ of the adsorbed molecules it is necessary, using the above methods, to calculate first the surface pressure φ. This calculation requires, unfortunately, an extrapolation of the adsorption isotherm to zero pressure.

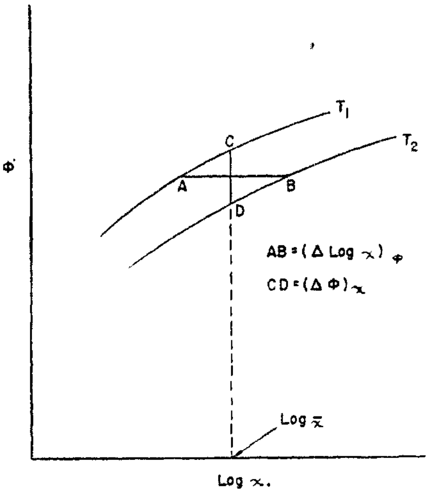

Fig. 1.—Schematic φ *versus* log x curves showing how Eq. (3) is applied.

However, in some systems it is possible to measure φ directly, as the difference between the surface tension of the pure adsorbent (*e.g.*, liquid mercury) and the surface tension of the adsorbent with adsorbed molecules on it.[5–7] In the present note, which is intended to be primarily thermodynamic rather than interpretive in nature, we calculate the energy, entropy and surface concentration of toluene, benzene and *n*-heptane adsorbed on liquid mercury, using the data of Kemball and Rideal.[5] These calculations are to be regarded as supplementary to the analysis given by Kemball and Rideal.[5]

We make the approximation throughout that the mercury surface is "unperturbed" by the adsorbed molecules. The thermodynamic calculations themselves are of course independent of any such assumption[8]; the approximation is introduced when one attributes the computed energy, entropy, etc., changes entirely to the adsorbed molecules.

Calculations

The two authors made independent calculations (circles and squares in the figures) starting with the same experimental data.[5] The procedure was as follows for each adsorbate.

Smooth curves are drawn through the experimental points of φ *versus* log x, where $x = p/p_0$, at 25 and 50°. For convenient values of φ, Δ log x is obtained from the smooth curves. We then calculate $\mathrm{H}'_{\mathrm{L}} - \mathcal{H}_{\mathrm{S}}$ from[8]

$$\mathrm{H}'_{\mathrm{L}} - \mathcal{H}_{\mathrm{S}} = -R\left(\frac{\partial \ln x}{\partial(1/T)}\right)_{\varphi} \tag{1}$$

where $\mathcal{H}_{\mathrm{S}} = \mathrm{E_S} + (\varphi/\Gamma)$, Γ is the surface concentration, and L' refers to the liquid state in equilibrium with vapor. Using average values[2] $\bar{x}$ and $\bar{T}$, the molar entropy relative to the liquid state is

$$\mathrm{S_S} - \mathrm{S}'_{\mathrm{L}} = \frac{\mathcal{H}_{\mathrm{S}} - \mathrm{H}'_{\mathrm{L}}}{\bar{T}} - R \ln \bar{x} \tag{2}$$

To calculate the surface concentration we employ

$$\Gamma = \frac{1}{RT}\left(\frac{\partial \varphi}{\partial \ln x}\right)_T = -\frac{1}{RT}\frac{(\partial\varphi/\partial T)_x}{(\partial \ln x/\partial T)_\varphi}$$
$$\cong -\frac{1}{RT}\frac{(\Delta\varphi)_x}{(\Delta \ln x)_\varphi} \tag{3}$$

For each value of log $\bar{x}$, $\varphi_{25°}$ and $\varphi_{50°}$ are read off the smooth φ *versus* log x curves (Fig. 1), giving $(\Delta\varphi)_x$. $(\Delta \log x)_\varphi$ is already available (Eq. (1)), so Γ may now be calculated from Eq. (3) for each $\bar{x}$ (and φ originally chosen). Finally, the molar

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[1] Presented at the American Chemical Society Meeting, New York, September, 1951.

[2] T. L. Hill, P. H. Emmett and L. G. Joyner, THIS JOURNAL, **73**, 5102, 5933 (1951).

[3] L. E. Drain and J. A. Morrison, American Chemical Society Meeting, New York, September, 1951.

[4] G. Jura and T. L. Hill, THIS JOURNAL, **74**, 1598 (1952).

[5] C. Kemball and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **187A**, 53 (1946). References to earlier work of this type are given by Kemball and Rideal.

[6] C. Kemball, *ibid.*, **187A**, 73 (1946).

[7] C. Kemball, *ibid.*, **190A**, 117 (1947).

[8] T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949); **18**, 246 (1950).

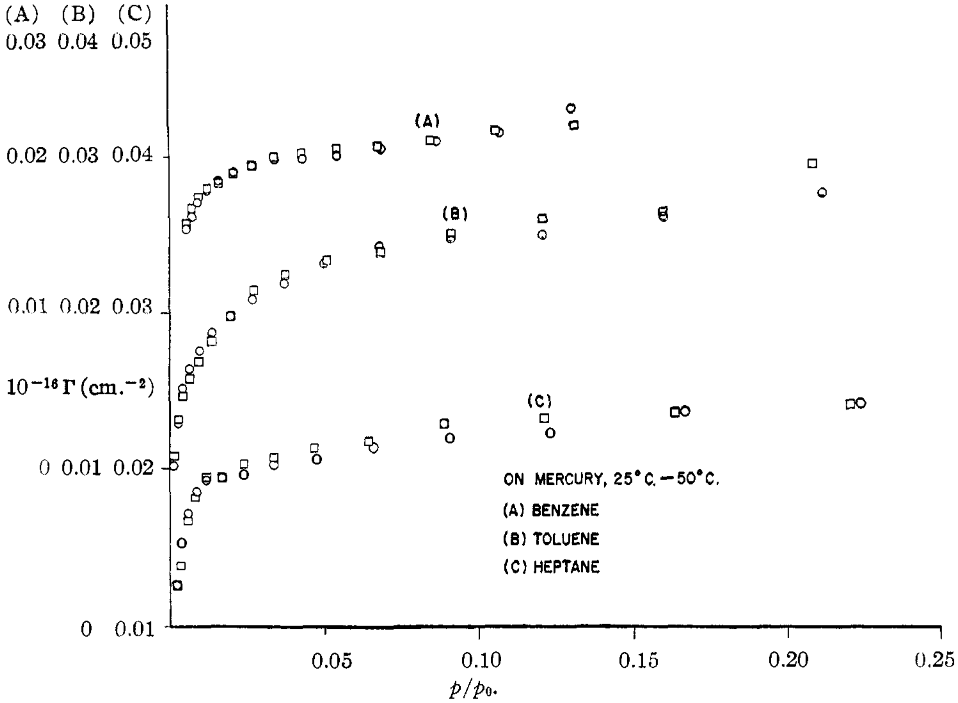

Fig. 2.—Adsorption isotherms of benzene, toluene and *n*-heptane on mercury, as deduced thermodynamically from surface tension measurements.

internal energy relative to the liquid state is computed from

$$\text{E}'_L - \text{E}_S = (\text{H}'_L - \mathcal{H}_S) + (\varphi/\Gamma) \qquad (4)$$

using the values of Γ just obtained.

Results and Discussion

Figure 2 shows the calculated adsorption isotherms for toluene, benzene and *n*-heptane. They are of conventional form; benzene and toluene show some indications of the beginning of multilayer adsorption at the highest pressures.

The energy and entropy of the adsorbed molecules, relative to the liquid state, are given in Figs. 3 and 4. At low coverages the order of decreasing strength (energy) of binding to the surface is toluene, benzene and *n*-heptane (the energies of vaporization, $\text{E}_G - \text{E}'_L$, are 8.7, 7.5 and 8.3 kcal./mole, respectively, at $\bar{T}$ = 310.1°K.). There is little variation in the energy of adsorption[9] of *n*-

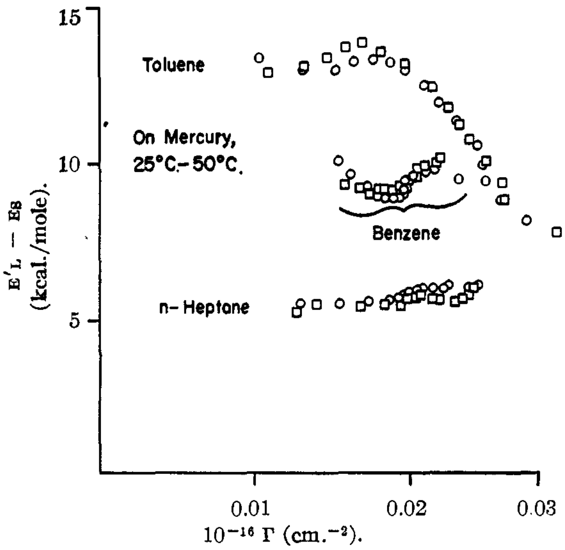

Fig. 3.—Molar internal energy, relative to the liquid state, of benzene, toluene and *n*-heptane molecules adsorbed on mercury.

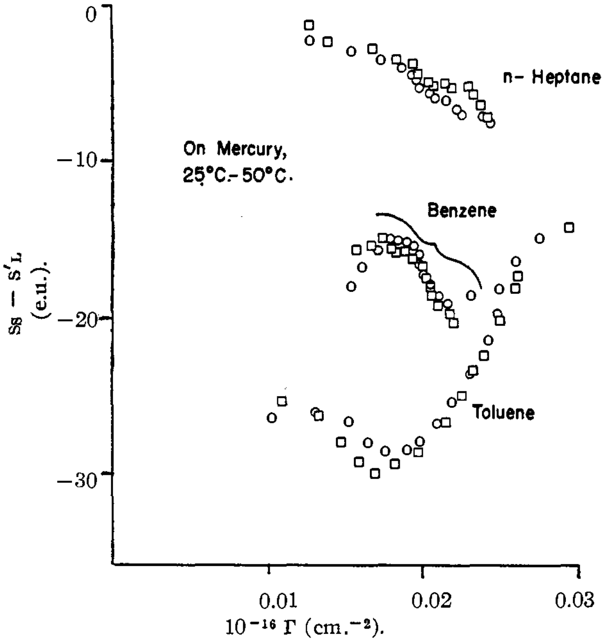

Fig. 4.—Molar entropy, relative to the liquid state, of benzene, toluene and *n*-heptane molecules adsorbed on mercury.

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[9] Strictly speaking, the *negative* of the energy of adsorption is the quantity under discussion but the terminology in the text is conventional.

heptane over the range of coverage investigated and the molar integral entropy of the adsorbed *n*-heptane decreases steadily with increasing coverage in a normal manner. The results for benzene are similar. The energy of adsorption of toluene is constant up to a coverage of 0.018 × 10^{16} molecules/cm.^{2}. It then falls by some 6 kcal./mole as the coverage is increased to 0.030 × 10^{16} molecules/cm.^{2}, and there is a corresponding rise in the molar entropy of the adsorbed material. Kemball and Rideal[5] suggested that at high coverages the adsorbed molecules were undergoing a change in orientation from "flat" to "vertical" adsorption and this was confirmed by the discovery of a small change in surface potential.[10] We believe that the fall in the energy and rise in the entropy of adsorption is consequent on this change of orientation. It is not likely to be due to the formation of a second layer because the area per molecule at the commencement of the change is 56 Å.^{2} while the area of a toluene molecule[5] is only about 37 Å.^{2}

Although the range Γ in Figs. 3 and 4 is small, we can say something about the limiting values of E_S and S_S as $\Gamma \rightarrow 0$ and $\Gamma \rightarrow \infty$ (assuming that Γ actually does approach infinity as $x \rightarrow 1$, as one expects below the critical temperature of the adsorbate on a non-porous adsorbent). As $\Gamma \rightarrow 0$, $E'_L - E_S \rightarrow$ finite and $S_S - S'_L \rightarrow +\infty$; as $\Gamma \rightarrow \infty$, $E'_L - E_S \rightarrow 0$ and $S_S - S'_L \rightarrow 0$.

The three substances show an interesting variation in freedom in the adsorbed state. Taking the vapor at one atmosphere pressure as the reference state, the experimental entropies of adsorption[11] of toluene, benzene and *n*-heptane are −51.3, −40.3 and −29.4 e.u. at coverages of 0.0135, 0.02 and 0.02 × 10^{16} molecules/cm.^{2}, respectively (roughly "corresponding states" judging from the energy and entropy curves). It is instructive to calculate the theoretical loss in entropy assuming that the molecules are forming a two-dimensional gas on the surface (neglecting interactions for simplicity) with free areas corresponding to the differences between the areas per molecule and the co-areas of the molecules as determined by Kemball and Rideal.[5] As the co-areas are 37, 35 and 33 Å.^{2}, respectively, the free areas are 37, 15 and 17 Å.^{2}. Using the usual equation for the three-dimensional translational entropy and the equation given by Kemball[6] for the two-dimensional translational entropy, the calculated losses are 19.6, 21.2 and 21.2 e.u., respectively. The fact that the experimental loss in entropy for *n*-heptane is only 8.2 e.u. greater than the value calculated on the model of the two-dimensional gas indicates that *n*-heptane has considerable freedom on the surface. Kemball[6] suggested that the adsorbed benzene might retain freedom to rotate in the plane of the ring but would lose the other two degrees of rotational freedom.[12] This model corresponds to a further loss of 16.9 e.u. making a total calculated loss of 38.1 e.u., which is to be compared with the experimental value of 40.3 e.u. The loss in entropy on adsorption of toluene is very much greater than the calculated value for the gaseous model. It is probable that the toluene is not freely mobile but it is not possible to suggest here what fraction of the loss of 51.3 e.u. is attributable to restriction of translation and what fraction to restriction of rotation (of the benzene ring and of the methyl group).

In this discussion we have ignored the small gain in entropy associated with the new vibrational degrees of freedom which must replace the lost degrees of translational and rotational freedom.

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[10] C. Kemball, *Proc. Roy. Soc.* (*London*), **201A**, 377 (1950).

[11] The values of s_G(1 atm.) − s'_L at $\bar{T}$ = 310.1°K. are 24.9, 23.3 and 24.4 e.u., respectively.

[12] See also J. W. Drenan and T. L. Hill, *J. Chem. Phys.*, **17**, 775 (1949).

Fischer Indole Syntheses with Polyphosphoric Acid

BY H. M. KISSMAN, D. W. FARNSWORTH AND B. WITKOP

RECEIVED MARCH 10, 1952

The successful application of polyphosphoric acid in cyclodehydration reactions[1,2] and Beckmann rearrangements[3] prompted us to try it in the Fischer indole synthesis especially in connection with those phenylhydrazones which are known to require drastic conditions for the elimination of ammonia and for indole ring closure.[4]

It was found that the use of polyphosphoric acid gave 2-phenylindole in good yields not only from acetophenone phenylhydrazone but also from a mixture of phenylhydrazine and acetophenone. A vigorous exothermic reaction and a color change from orange to dark brown took place when such a homogeneous mixture of phenylhydrazine, the ketone and polyphosphoric acid was heated to 120°. The indole could be isolated in fairly pure form by adding water to the reaction product.

An extension of this method to the preparation of other indole derivatives showed that it had fairly wide applicability. The aryl- and alkylsubstituted indoles shown in Table I were prepared from the corresponding ketones, phenylhydrazine and polyphosphoric acid. The reaction involving N-methylphenylhydrazine and acetophenone was carried out in order to see whether polyphosphoric acid could be used for the synthesis of N-substituted indoles. As expected, 1-methyl-2-phenylindole was obtained in good yield from this reaction. The use of isobutyrophenone and phenylhydrazine led to the isolation of 3,3-dimethyl-2-phenylindolenine showing that the polyphosphoric acid procedure could also be applied to the synthesis of indolenines.

In order to avoid tar formation it was very important, in all cases, to cool the reaction mixture immediately after the reaction had started. The maximum temperatures used in these reactions are shown in Table I. It is probable that the yields of some of these indole derivatives could be improved by changing these temperature conditions. The

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[1] H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2962 (1950).

[2] E. C. Horning, J. Koo and G. N. Walker, *ibid.*, **73**, 5826 (1951).

[3] E. C. Horning and V. L. Stromberg, *ibid.*, **74**, 2680 (1952).

[4] R. L. Shriner, W. C. Ashley and E. Welch, *Org. Syntheses*, **22**, 98 (1942).