in the cell. The relation of these results to the problem of the enhanced O^{18} content of the atmosphere is discussed, and a theory for the latter is given which seems for the first time to be quantitatively possible.

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[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AND THE RESEARCH LABORATORY OF GODFREY L. CABOT, INC.]

Heats of Adsorption and Molecular Configuration. The Pentanes on Carbon Black

BY R. A. BEEBE,[1] G. L. KINGTON,[1] M. H. POLLEY[1] AND W. R. SMITH[2]*

In an investigation of the factors which contribute to the energy of binding between physically adsorbed molecules and a solid surface, it is obviously necessary to consider the nature of the adsorbate molecules as well as the state of the solid surface. Earlier work[3] which has been reported from these Laboratories has shown that the heats of physical adsorption for a specific gas such as nitrogen or butane may vary considerably on different carbon surfaces such as Spheron 6 and Graphon carbon blacks.

If we limit our consideration to a single solid surface, we still find instances of marked differences in the binding energies, as shown by differences in the heats of physical adsorption, for different adsorbates on the same adsorbing surface. These differences may be due to such obvious factors as difference in molecular weight as illustrated by the heats of adsorption of *n*-butane and *n*-pentane on carbon black,[3] or to difference in polarizability of the adsorbate molecules as in the comparison of the heats of adsorption of *n*-butane and 1-butene on silica gel.[4] However, in certain instances, these differences in binding energy appear to arise from less obvious causes. For instance it has been found that the heat of adsorption for nitrogen exceeds that for oxygen on a relatively bare anatase surface[5] by about 1 kcal. per mole of adsorbate although molecular weight considerations would lead one to predict the reverse relationship in the heat values.

In the present investigation, we have chosen to work with the two isomeric C_5 hydrocarbons: *n*-pentane and neopentane (2,2-dimethylpropane), on the same carbon black surface at 0°. In these two hydrocarbons we have adsorbates with identical molecular weights and closely similar chemical properties, but with different geometric configurations. Although cyclopentane is not a true isomer of the other two pentanes studied, it has been included in the present work. Our experimental results show that there are marked differences in the energies of binding of these C_5 hydrocarbons to the carbon black surface, which can be plausibly explained on the basis of molecular configuration.

Experimental

Materials.—The carbon black adsorbent was a sample of a commercial black designated as Spheron 6. The properties of this pigment, which have been extensively studied, have been described in detail in previous publications.[3] Further studies on carbon black structure have been made more recently by Hall with dark-field illumination in the electron microscope.[6]

The *n*-butane and neopentane were Phillips research grade; the *n*-pentane and cyclopentane were Phillips pure grade. All these hydrocarbons were of warranted purity 99 mole per cent. or better. Any air which might have been introduced during transfer was removed by evacuating the system while the hydrocarbon was frozen out in a side trap at −195°. This operation was followed by several bulb to bulb distillations with evacuation between distillations.

Apparatus.—The apparatus used in this work has been previously described.[3] In order to be as certain as possible about the value for the heat capacity of the calorimeter we have made altogether seventeen heat calibration determinations. The probable error of the mean for these calibrations was 0.37%.

Results and Discussion

Altogether, ten successful heat runs were carried out at 0° on two samples from the same batch of Spheron 6 carbon black. It was possible to determine the adsorption isotherms simultaneously with the calorimetric measurements. The results of these experiments are shown in Figs. 1 and 2.[7] B. E. T. plots of the isotherm data yielded straight lines up to 0.25 relative pressure in all cases. From these plots it was possible to determine the values of V_m and of c of the B. E. T. equation which are given in Table I.

TABLE I

Adsorbate	V_m, cc./g.	c	σ, sq. Å./molecule
n-Butane	9.2	40	45
n-Pentane	8.0	58	53
Neopentane	7.3	53	57
Cyclopentane	8.8	23	47

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[3] (a) Beebe, Biscoe, Smith and Wendell, THIS JOURNAL, **69**, 95 (1947); (b) Beebe, Polley, Smith and Wendell, *ibid.*, **69**, 2294 (1947).

[4] Beebe and Smith, *Ind. Eng. Chem.*, **41**, 1431 (1949).

[5] Kington, Polley, Smith and Beebe, forthcoming publication.

[6] Hall, *J. Applied Phys.*, **19**, 271 (1948).

[7] (a) The values of E_L, the heats of liquefaction of the hydrocarbons under investigation, are indicated at the right of Fig. 2; (b) the order of the experiments was as follows: Run 82, *n*-butane; Run 83, *n*-pentane; Run 84, neopentane; Run 85, neopentane; Run 86, cyclopentane; Run 87, *n*-butane; Run 97, *n*-butane; Run 98, *n*-butane; Run 99, *n*-pentane; Run 100, cyclopentane. Sample 1 of the carbon black was used in Runs 82–87; Sample 2, in Runs 97–100.

It is noteworthy that, as might be expected in adsorption processes having relatively low c values, no definite point on any of the isotherms could very well be designated as the point B of Emmett and Brunauer; *i. e.*, the point at which the monolayer may be considered to be filled. While the significance of the value V_m is in some doubt in cases like this, it is still true that V_m is a reproducible number which is characteristic of the particular process under study. Knowing the specific surface area from nitrogen adsorption data (σ_{N_2} = 16.2 Å.^{2}) and the values of V_m for the different hydrocarbons, it has been possible to calculate the values of σ, given in Table I, which represent the areas occupied per molecule. In previous publications[3] we have included the values of E_1 calculated from the B. E. T. equations. Such data, which can of course be calculated from the c values, are not included here. The relationship between these E_1 values and the calorimetrically determined heats of adsorption is essentially the same as in the previous work.

A comparison of the isotherms for Runs 82 and 87, using *n*-butane, showed that there had been no detectable change in adsorptive capacity in Sample 1 of the carbon black during Runs 82–87. This gave evidence that there had been no change in the carbon surface during the series of runs and that the method of outgassing at 200° between runs was adequate for the removal of previously adsorbed hydrocarbons. Moreover a duplication in the isotherms for Runs 82, 87, 97 and 98, indicated identical adsorptive capacity for Samples 1 and 2 of the carbon black.[8]

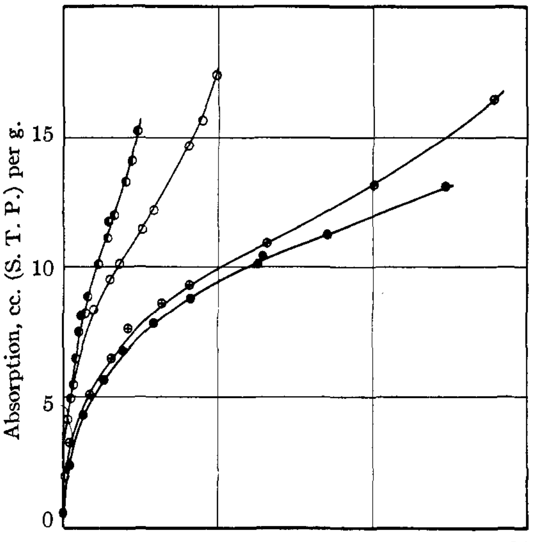

Fig. 1.—Isotherms at 0°, hydrocarbons on Spheron 6 carbon black: Runs 82, 87, 97, 98, *n*-butane ●; Run 83, *n*-pentane, O; Runs 84, 85, neopentane, ⊕; Runs 86, 100, cyclopentane, ◐. The vapor pressures at 0° for these hydrocarbons in the order listed are 77.54, 18.34, 53.23 and 10.66 cm., respectively.

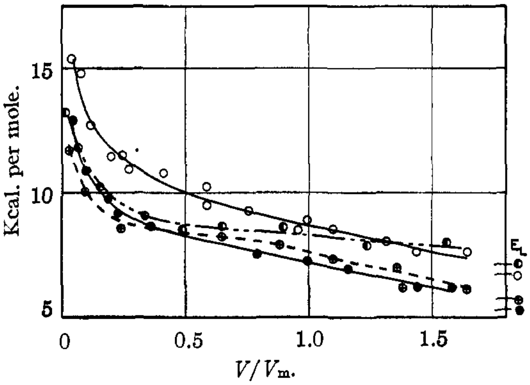

Fig. 2.—Differential heats of adsorption at 0°, hydrocarbons on Spheron 6 carbon black: Runs 82, 87, 97, 98, *n*-butane, ●; Run 83, *n*-pentane, O; Runs 84, 85, neopentane, ⊕; Runs 86, 100, cyclopentane ◐.

The differential heat curves of Fig. 2 are of special interest. In the first two-thirds of the estimated monolayer, the differential heats for neopentane and cyclopentane are very substantially lower than those for *n*-pentane. A comparison of these curves with that for butane on a relatively bare carbon black surface shows that the cyclopentane curve is almost identical with that for butane, and that the neopentane gives an even lower heat than butane despite its higher molecular weight. These observations appear to be most readily explained on the basis of the molecular configurations of the hydrocarbons under investigation. If we consider the differential heats of adsorption per mole of adsorbate at 0.05 coverage

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(8) (a) It is worthy of note that the differential heats for both butane and pentane, on the Spheron 6 carbon black used in the present study, run about 10% lower than those previously reported for these adsorbates on another sample of Spheron 6 black.[3] Since the hydrocarbons used in both investigations were Phillips Research Grade, and since there was a similar discrepancy for both the butane and the pentane between the present and the earlier work, it seems improbable that this could be attributed to any impurities in the hydrocarbons used. Whether the discrepancy was due to a difference in the carbon samples used in the present work and in the earlier work, or whether to some unknown error, possibly in the electrical calibration for the heat capacity of the calorimeter in the previous research, we are unable to decide. It should be pointed out, however, that even if the earlier results as reported were too high by 10%, this would not vitiate the conclusions which were drawn from those results, for lower heats in the earlier work would constitute even more conclusive evidence for the absence of an appreciable amount of chemisorption. Moreover, the comparison of the heats for saturated and unsaturated hydrocarbons would depend on relative rather than absolute values. In view of the above discussion it is gratifying that the results of the present work in Runs 82-87 and 97-100 are consistent with each other as indicated by the duplication of the heat data with butane in Runs 82, 87, 97 and 98. (b) In the previous publication on hydrocarbon adsorption on carbon blacks attention was called in note 13 to the *apparent levelling off* of the heats in the second layer at a value of considerably in excess of E_L. In our present work we have extended the heat measurements with *n*-butane somewhat beyond the second layer, although the heat values are not shown beyond v/v_m = 1.6 in Fig. 2. Although we have less confidence in our heat data at such high quantities adsorbed than we have at low coverage, we believe that our present experimental evidence is sufficient to indicate that heats of adsorption do *eventually approach the heat of liquefaction rather than levelling off at a value higher than* E_L, as previously suggested.

we find that *n*-pentane and *n*-butane have the approximate values 12 and 15 kcal., respectively. As an approximation to the truth, we may assume that these molecules are adsorbed with their major axes lying in the plane of the adsorbing surface and that the contribution to the heat of van der Waals adsorption is approximately 3 kcal. per $-CH_2$ group thus accounting for the difference of 3 kcal. between the C_4 and C_5, and for total contributions of 12 and 15 kcal. for the two hydrocarbons respectively at 0.05 coverage.

If one builds Hirschfelder three-dimensional molecular models of *n*-pentane and neopentane it is apparent that the *n*-pentane could be so placed on a plane surface as to bring all its $-CH_2$ or $-CH_3$ groups into close contact. On the other hand, in the case of the neopentane, three $-CH_3$ groups could make close contact with the surface; the central carbon atom would be near enough to make some contribution to the total attraction between the surface and the adsorbed molecule, but the fourth $-CH_2$ group would be so far removed from the surface as to make relatively little contribution to the van der Waals forces, since such forces are inversely proportional approximately to the cube of the distance of the group from the surface. While it is obviously naive to assume that the surface is truly planar from the point of view of the adsorbate molecule, yet the molecular configurations of *n*-pentane and neopentane would appear to account for relatively lower heats of the latter hydrocarbon even with a molecularly rough surface. Of course the *n*-pentane molecules would be able to adapt their shape to a rough surface more readily than would those of neopentane.

Cyclopentane has been shown to consist essentially of rigid molecules in the form of puckered rings.[9] It seems reasonable that such rigid molecules would fit only imperfectly on an even slightly rough surface, thus accounting for the low heats of adsorption compared to *n*-pentane. Presumably, however, the molecules of this hydrocarbon are capable of closer contact than are those of neopentane.

Although it is possible to relate the shape of the neopentane molecule to the low heat of adsorption of this hydrocarbon, it should be observed that the value of σ for neopentane reported in Table I appears to be anomalously high. Thus with only three $-CH_3$ groups in contact with the surface and one $-CH_3$ group definitely not in contact, we have a σ value of 57 sq. Å. compared to 45 for *n*-butane and 53 for *n*-pentane. We are unable to offer a very plausible explanation of this observation. Of course it is possible that the B. E. T. method does not give a true value of the volume of gas required to fill the monolayer in this case. A similar unexplained high value in σ has been reported in the case of krypton on several adsorbents.[10]

Summary

1. The isotherms and calorimetric heats of adsorption have been determined at 0° for *n*-butane, *n*-pentane, neopentane and cyclopentane on a sample of carbon black which has been extensively used for previous adsorption studies.

2. It is found that at 0.05 coverage of the surface, the contribution per $-CH_2$ group of the normal hydrocarbons is approximately 3 kcal. per mole.

3. It is found that the neopentane and the cyclopentane have heat values in which the contribution per $-CH_2$ or $-CH_3$ group is less than the 3 kcal. encountered with the normal hydrocarbons.

4. The explanation is suggested that the differences in the energies of binding of these pentanes as indicated from the heat measurements may be attributed to differences in geometric fit of their molecules to the carbon black surface.

AMHERST, MASS. RECEIVED JULY 1, 1949

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[9] (a) Aston, Schuman, Fink and Doty, THIS JOURNAL, **63**, 2029 (1941); (b) Spitzer and Pitzer, *ibid.*, **68**, 2537 (1946); (c) Spitzer and Huffman, *ibid.*, **69**, 211 (1947).

[10] Beebe, Beckwith and Honig, THIS JOURNAL, **67**, 1554 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Catalysis of the Reaction of Carbon Monoxide with Iodine in Acid Solution[1]

BY WILLIAM MARSHALL MACNEVIN* AND WILLIAM NEUTON CARSON, JR.[2,3]

The reaction between carbon monoxide and iodine in acid solution has not been reported in the literature. According to the free energy change, $\Delta F^0_{298.10} = -33{,}835$ cal./mole, the reaction should occur readily. Preliminary experiments indicated that it could be catalyzed appreciably. A more extensive study of catalysts and conditions has therefore been made and is reported in this paper.

Preparation of Carbon Monoxide.—Carbon monoxide was prepared in an all glass apparatus by bubbling anhydrous formic acid into concentrated sulfuric acid at 100°. The gas was scrubbed with chloroform, 50% potassium hydroxide solution and alkaline pyrogallol. The apparatus was designed so the generator could be emptied of spent sulfuric acid and refilled without introducing air. The gas was stored over water.

Iodine Reaction.—The iodine reactor vessel consisted of a 200 mm. × 25 mm. Pyrex tube sealed at the lower end. Carbon monoxide was led through a 7-mm. tube sealed

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* Harvard University A.M. 1932.

[1] From a thesis presented by William N. Carson, Jr., to the Graduate School of the Ohio State University in partial fulfillment of the requirements for the degree Doctor of Philosophy, June, 1948.

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