of LF data) taking values of $v$ and $T \, dP/dT$ from ref. 14 was 0.05% greater than that obtained using both HF and LF data (second experimental method). Between these two results falls a value determined with considerable care by Osborne, Stimson and Ginnings[14] using calorimeters of a different type. This agreement was undoubtedly somewhat fortuitous since the probable error of the enthalpy measurement is estimated as being 0.2%, except at temperatures below 100° in which range it is greater. This estimate is based upon suspected systematic errors of which the largest

(14) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards,* **23**, 261 (1939).

is the error involved in measuring the temperature of the sample in the furnace.

## Summary

1. There has been described the experimental technique of measuring the enthalpy of saturated liquids from 0° to near the critical point utilizing an ice calorimeter.

2. The enthalpy, entropy and specific heat of saturated liquid *p*-xylene have been determined in the range, 0° to 300°.

3. The heat of fusion of *p*-xylene at 0° has been determined.

WASHINGTON, D. C. RECEIVED MAY 5, 1947

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# Heats of Adsorption on Carbon Black. II

BY R. A. BEEBE,[1] M. H. POLLEY,[1] W. R. SMITH[2] AND C. B. WENDELL[2]

The results of an experimental investigation of the heats of low temperature van der Waals adsorption of nitrogen, oxygen and argon on a series of carbon blacks of varying rubber reinforcing ability have been reported in a recent publication.[3] In addition to their relation to the problem of rubber reinforcement, these results have some significance from a fundamental point of view. The carbon blacks used in the present study are well defined, highly reproducible, non-porous materials of high surface area. There is a considerable body of information[4] available concerning the structure of the underlying solid and the extent of adsorbent surface based on X-ray diffraction and electron microscope studies. The heat measurements with the elementary gas adsorbates have revealed interesting differences in the state of surface of the various blacks, differences which permit some degree of correlation with rubber reinforcing abilities of the blacks. Obviously any such correlation would give promise of greater significance with adsorbates more nearly like rubber in chemical composition. For that reason we have undertaken a study of the heats of adsorption at 0° of several saturated and unsaturated hydrocarbons of low molecular weight which can be handled conveniently in the vapor state.[5]

(1) Amherst College, Amherst, Mass.

(2) Godfrey L. Cabot, Inc., Boston, Mass.

(3) Beebe, Biscoe, Smith and Wendell, THIS JOURNAL, **69**, 95 (1947).

(4) (a) Emmett and DeWitt, *Ind. Eng. Chem., Anal. Ed.,* **13**, 28 (1941); (b) Smith, Thornhill and Bray, *Ind. Eng. Chem.,* **33**, 1303 (1941); (c) Wiegand and Ladd, *Rubber Age,* **50**, 431 (1942); (d) Warren, *J. Chem. Phys.,* **2**, 551 (1934); (e) Biscoe and Warren, *J. Appl. Phys.,* **13**, 364 (1942).

(5) The simple mono- and di-olefins selected for study are, of course, far removed from the complex, unsaturated high polymer, rubber. The danger of drawing analogies between the two has been amply discussed by Farmer [for example, see Farmer, "Advances in Colloid Science II," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 301-302]. On the other hand, rubber is hardly suitable

## Experimental

**Materials.**—The five samples of carbon black, previously studied,[3] were used also in the present experiments. They include three commercial blacks, Spheron Grade 6 (MPC), Sterling S (SRF), and Sterling L (HMF).[3] The first of these is a reinforcing channel black and the other two are typical furnace blacks.[6] The list is completed by a sample of Spheron Grade 6 heated to 927° to remove most of the chemisorbed surface oxides ("devolatilized" Grade 6), and a sample of Grade 6 heated to "graphitizing" temperatures 2800-3300° and designated as Graphon. Prior to each adsorption run, the black under investigation was outgassed at 200°, a temperature sufficient to remove physically occluded air and moisture without desorption of the chemisorbed gases normally present on the carbon surface.

The butane and 1-butene were research-grade hydrocarbons purchased from the Phillips Petroleum Company. All other hydrocarbons used in the investigation were kindly supplied by the Esso Laboratories, Standard Oil Development Company, and were of warranted purity of at least 99%. Any air introduced during transfer was removed by evacuation of the system while the hydrocarbon was frozen out in a side trap immersed in liquid nitrogen, followed by several bulb to bulb distillations.

**Apparatus.**—The calorimeter used in this work was essentially the same as that already described,[3] although a somewhat more convenient method was devised for inserting the electrical calibration unit. The adsorption apparatus used in conjunction with the calorimeter was redesigned with mercury "cut-offs" to prevent contact of the hydrocarbons with stopcock grease. This modified apparatus has been described in a separate publication.[7] An ice-bath served to produce a uniform constant temperature around the calorimeter.

## Results and Discussion

The experimental results are presented in Figs. 1-7 and Table I. Figures 1 and 2 give the B.E.T.[8]

as an adsorbate in the present calorimetric procedure. Accordingly, simple hydrocarbons of chemical, if not structural, similarity to rubber were chosen for initial study, the possible use of more complex systems being reserved for future investigation.

(6) Cohan, *Chem. Eng. News,* **23**, 2078 (1945).

(7) Wendell, *Ind. Eng. Chem.,* **18**, 454 (1946).

(8) B.E.T. has reference to the method of Brunauer, Emmett and Teller based on the theory of multilayer adsorption due to these authors [THIS JOURNAL, **60**, 309 (1938)].

TABLE I

DATA DERIVED FROM THE B.E.T. PLOTS FOR HYDROCARBONS ON CARBON BLACKS AT $0°$

| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) |
|---|---|---|---|---|---|---|---|
| | | | $\Sigma$ for $N_2$ | | | $E_1 - E_L$ | $E_1' - E_L$ |
| Sample | Adsorbate | $v_m$, cc./g. | $m^2$/g. | $\sigma$, sq. Å. | $p_0$, mm. | cal./mole | cal./mol |
| Spheron Grade 6 | $n$-butane | 9.23 | 111.2 | 45.1 | 775.4[b] | 2070 | 5230 |
| Spheron Grade 6 | 1-butene | 10.20 | 111.2 | 40.6 | 965.2[b] | 2165 | 5020 |
| Spheron Grade 6 | cis-2-butene | 10.79 | 111.2 | 38.5 | 660.0[b] | 1985 | 5520 |
| Spheron Grade 6 | trans-2-butene | 12.42 | 111.2 | 33.4 | 734.9[b] | 2020 | 4990 |
| Spheron Grade 6 | $n$-pentane | 8.20 | 111.2 | 50.6 | 183.4[c] | 2150 | 6290 |
| Spheron Grade 6 | 1-pentene | 8.67 | 111.2 | 47.8 | 257.9[d] | 2200 | 6320 |
| Spheron Grade 6 | 2-pentene[a] | 9.92 | 111.2 | 41.8 | 181.3[d] | 1855 | 6440 |
| Spheron Grade 6 | Tri-meth. ethylene | 8.88 | 111.2 | 46.7 | 164.7[e] | 2090 | 5600 |
| Spheron Grade 6 | Butadiene | 12.61 | 111.2 | 32.9 | 892.6[f] | 2120 | 5890 |
| Spheron Gr. 6 "devol." | 1-butene | 11.21 | 120.8 | 40.1 | 965.2 | 2308 | 5420 |
| Graphon | $n$-butane | 7.83 | 83.4 | 39.7 | 775.4 | 2860 | 4070 |
| Graphon | 1-butene | 8.22 | 83.4 | 37.8 | 965.2 | 3100 | 3630 |
| Sterling S | $n$-butane | 2.06 | 24.2 | 43.7 | 775.4 | 2021 | 4390 |
| Sterling S | 1-butene | 2.33 | 24.2 | 38.7 | 965.2 | 1884 | 3540 |
| Sterling L | $n$-butane | 2.97 | 33.0 | 41.4 | 775.4 | 2185 | 3590 |
| Sterling L | 1-butene | 3.19 | 33.0 | 38.6 | 965.2 | 2090 | 2930 |

[a] This was a mixture of the cis- and trans-forms.   [b] Wackher, Linn and Grosse, *Ind. Eng. Chem., Ind. Ed.*, **37**, 464 (1945).   [c] American Petroleum Institute Research Project 44.   [d] These values were determined experimentally.   [e] Lamb and Roper, THIS JOURNAL, **62**, 806 (1940).   [f] Wood and Higgins, *India Rubber World*, **107**, 475 (1943).

plots using data obtained during calorimetric runs for the four- and five-carbon hydrocarbons on Spheron Grade 6. Some pertinent data derived from the B.E.T. plots are given in Table I. In column 3 of this table are listed the volumes, $v_m$, of hydrocarbon vapor at N.T.P. in the B.E.T. monolayer per gram of black. The specific surface areas, $\Sigma$, listed in column 4, have been determined by the B.E.T. method using nitrogen adsorption at $-195°$, assuming that 16.2 sq. Å. is the area occupied by the nitrogen molecule. Knowing the values of $v_m$ listed in column 3 and the corresponding specific surface areas of column 4, it is possible to calculate the values of $\sigma$, the area occupied by the molecule of the hydrocarbon in question. These areas are given in column 5.

butane molecule adsorbed on a solid surface. These authors obtained the value 32.1 sq. Å. when they based their calculation on the assumption of liquid close packing of spherical molecules, and 32.0 sq. Å. was obtained by assuming a solid monolayer with the butane molecules lying flat on the surface, each occupying an oblong 4.3 Å. on one side and 7.45 Å. on the other. Similar calulations for $n$-pentane yield 35.6 and 37.6 sq. Å. for liquid and solid films, respectively.
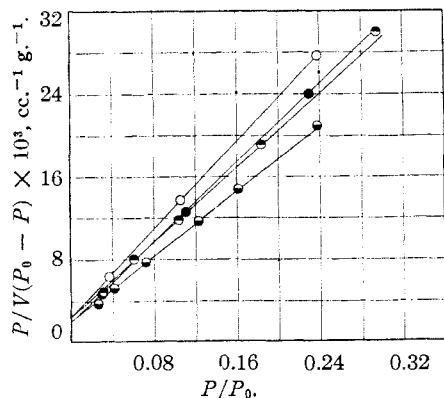


Fig. 1.—B. E. T. plots: run 44, $n$-butane ○; run 43, 1-butene ●; run 58, cis-2-butene ◑; run 57, trans-2-butene ◐.



Fig. 2.—B. E. T. plots: run 66, $n$-pentane ○; run 63, 1-pentene ●; run 64, 2-pentene (cis and trans isomers) ◑; run 62, trimethylethylene ◓.

It is worthy of note that Emmett and Brunauer[9] have calculated the area occupied by the $n$-

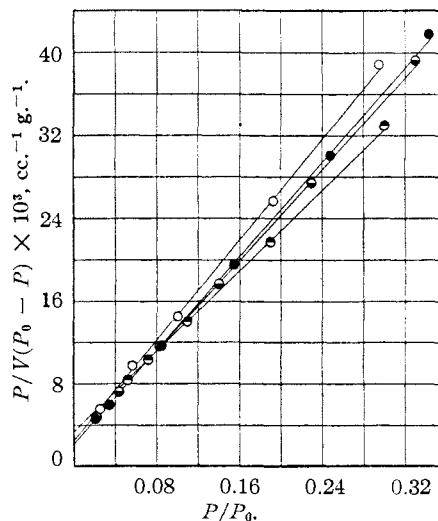(9) Emmett and Brunauer, THIS JOURNAL, **59**, 1559 (1937).

Because the assumption that the hydrocarbon molecules in the liquid state are spherical in shape is obviously tenable only as a first approximation, we have calculated areas per molecule based on

the assumption that the molecules lie flat on the surface in the liquid state making use of recent data from several sources on the dimensions of hydrocarbon molecules in the liquids.[10] Such calculations give values of $\sigma$ from 35.4 to 40.0 sq. Å. for butane, and 41.1 to 46.5 sq. Å. for pentane. Comparing these with the experimental values 45.1 and 50.6 sq. Å. for these two hydrocarbons on Grade 6 carbon black, we may conclude that the molecules are reasonably near to being close packed especially if we bear in mind that the values of $\epsilon$, on which the experimental $\sigma$ values depend, were found by assigning the somewhat arbitrary value of 16.2 sq. Å. to the nitrogen molecule, and were determined by use of nitrogen molecules which could more completely cover a somewhat irregular adsorbing surface than could the larger hydrocarbon molecules. This point of view is supported by the lower experimental value of $\sigma$ obtained with butane on Graphon indicating a closer packing on the more regularly crystalline graphitic structure of this adsorbent surface. A similar low value of $\sigma$ was observed by Livingston[11] for heptane on graphite.

In plotting the data of Figs. 1 and 2, the $p_0$ values were taken from various available sources as designated in column 6 of Table I. Deviations from the gas laws were estimated to be less than 1% for any of the hydrocarbons up to a relative pressure of 0.20. For the last few points at higher relative pressures estimated corrections were considered, although sufficient data for exact corrections were not at hand for the pentane and pentenes.

In column 7, are listed the values of $E_1 - E_L$ as calculated from the B.E.T. plots[3]; and in column 8 we have recorded the values of $E_1' - E_L$ where $E_1'$ is the calorimetrically determined integral heat of adsorption for the first layer and $E_L$ is the heat of liquefaction of the hydrocarbon.
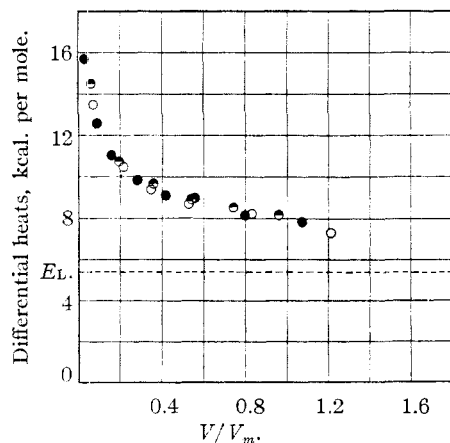


Fig. 3.—Heats of adsorption at 0°, n-butane on Spheron Grade 6: run 41 O; run 44 ●; run 54 ◐.

(10) Mark, "High Polymers," Vol. 2, Interscience Publishers, Inc., New York, N. Y. 1940, p. 191.

(11) Livingston, THIS JOURNAL, 66, 569 (1944).

Twenty-three successful heat runs have been carried out with the hydrocarbon adsorbates on the carbon black samples. The results of the differential heat measurements are given in Figs. 3-7.

To give some idea of the reproducibility of successive measurements the data from three heat runs for n-butane on Spheron Grade 6 black are plotted in Fig. 3. Figure 4 presents the results of heat runs on the same sample of Spheron Grade 6 in which the adsorbates were successively n-butane, 1-butene, cis-2-butene, and trans-2-butene. The nearly identical values of the heats for
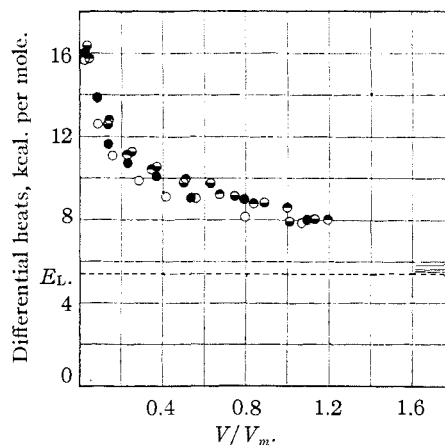


Fig. 4.—Heats of adsorption at 0°, n-butane and butenes on Spheron Grade 6: run 44, n-butane O; run 43, 1-butene ●; run 58, cis-2-butene ◐; run 57, trans-2-butene ◑.

these four hydrocarbons as well as for 1,3-butadiene[12] indicate that the binding energy is not appreciably different whether the saturated or unsaturated hydrocarbon is used, nor is it greatly affected by the position of the double bond or the isomeric forms of the 2-butenes. Similar conclusions may be drawn from the relative behavior of pentane and the pentenes for which the results are shown in Fig. 5. It should be mentioned that in the series of experiments with the 5-carbon adsorbates and the butadiene, there was some apparent decrease in specific surface area. For instance, runs 54–67 were carried out without changing the sample of Spheron Grade 6 black and in runs 62–67 the following adsorbates were used in succession, trimethylethylene, 1-pentene, cis- and trans-2-pentenes (mixture), n-pentane, 1,3-butadiene. Following outgassing of the adsorbate from run 67, the n-butane isotherm was measured; $v_m$ as determined from the B.E.T. plot was then 11% lower than that determined on a fresh sample of black. Thus the 200° outgassing temperature had been insufficient completely to

(12) With 1,3-butadiene used in run 67 discussed below, the differential heats were essentially the same as with the butane and the butenes. For reasons given below, it was believed that the surface had undergone a slight change before or during the butadiene run. The results of run 67 should therefore not be given the same weight as should the other runs with the 4-carbon compounds. However, it is fair to say that the presence of the conjugated double bond system appears to have no great effect on the heat values.

remove the adsorbate from the carbon black, after adsorptions with the 5-carbon compounds and the butadiene. This effect may of course have been due to a slow polymerization especially in the case of the butadiene with the production of compounds of higher molecular weight which would be less easily desorbed.
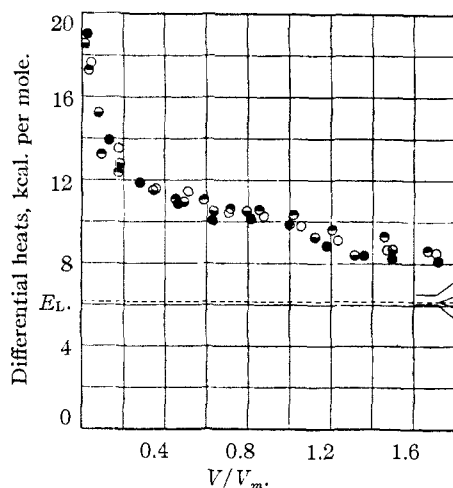


Fig. 5.—Heats of adsorption at 0°: run 66, $n$-pentane O; run 63, 1-pentene ●; run 64, 1-pentene (cis and trans isomers) ◐; run 62, trimethylethylene ◑.

Using 1-butene as adsorbate, the relative behavior of the four blacks, Spheron Grade 6, "devolatilized" Grade 6, Graphon, and Sterling S, is illustrated in Figs. 6 and 7. Similar results were obtained with $n$-butane, although the heat data for the latter adsorbate are not shown in Figs. 6 and 7. A single run with 1-butene on Sterling L gave essentially the same heat curve as that shown for Sterling S in Fig. 7.

The general conclusions to be drawn from the present investigation are remarkably similar to those of our previous publication[3] in which nitrogen was the adsorbate most thoroughly studied.[13] With the present hydrocarbon adsorbates, we note a sharp difference in the nature of the differential heat curves on the completely reinforcing blacks such as Spheron Grade 6 and "devolatil-

(13) In the case of the hydrocarbons, the heats appear to level off in the second layer at a value considerably in excess of $E_L$. This behavior of the hydrocarbons, which is most clearly evident in the heats of the C₅ adsorbates on Spheron Grade 6 shown in Fig. 5, is in sharp contrast to that of the elementary gases previously studied.[3] For example, at $v/v_m = 1.5$, the heat of adsorption for the single run on $n$-pentane is over 40% in excess of $E_L$, while that for nitrogen, based on an average from several runs, for $v/v_m = 1.5$, is only about 15% in excess of $E_L$. It is seen from Fig. 5 that the other C₅ hydrocarbons behave in a similar manner. Unfortunately the measurements with the C₄ adsorbates were not extended very far into the second layer, but the results we have obtained appear to indicate that the C₄ adsorbates are intermediate between the C₅ hydrocarbons and the elementary gases as regards the leveling off of the heat curves. Although we have considered possible explanations of the above observations, we prefer not to offer any of them at this time. It is hoped that further systematic experimental study, now in progress, of the heats of adsorption of straight and branched chain hydrocarbons may yield data which will be useful in interpreting the shapes of the differential heat curves.
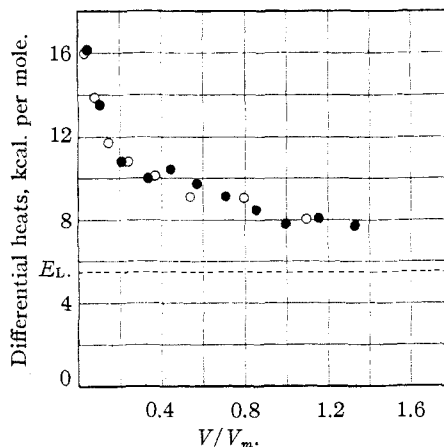


Fig. 6.—Heats of adsorption at 0°, 1-butene on Spheron Grade 6 and Spheron Grade 6 "devolatilized": run 43 Spheron Grade 6 O; run 37, Spheron Grade 6 "devolatilized" ●.
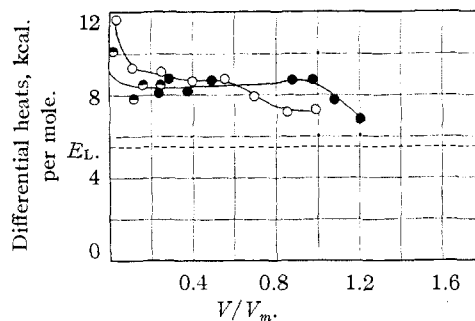


Fig. 7.—Heats of adsorption at 0°, 1-butene on Sterling S and Graphon: run 52, Sterling S O; run 49, Graphon ●; run 51, Graphon ◑.

ized" Grade 6 as compared to the lower reinforcing Graphon and the furnace blacks. Moreover we find little difference between the heats on the Grade 6 and Grade 6 "devolatilized" samples, indicating, as was also the case with nitrogen adsorption, that the removal of chemisorbed oxygen from the carbon surface had little effect on the strength of the forces operative between the surface of the adsorbent and the adsorbate molecules in the monolayer.

The heats appear to give little evidence of chemisorption. Although, at first thought, initial heat values of the order of 16 to 19 kcal. per mole might seem too high to be attributed solely to van der Waals adsorption, it is important to bear in mind that the molecules are doubtless lying flat on the surface and the heat of adsorption per —CH₂ or =CH group is then about 4 kcal. per mole. It is further noted that on an "active black" such as Grade 6 Spheron, the initial heats of adsorption with the hydrocarbon adsorbates are just about three times the heats of liquefaction; this ratio is almost identical with that obtained in the case of the van der Waals adsorption of nitrogen near its boiling point.[3]

It is especially noteworthy that we find no marked differences on any of the blacks between the differential heats for the saturated hydrocarbons and for the corresponding unsaturated compounds.

The rubber reinforcing properties of the carbon blacks, as discussed in the previous publication,[3] generally parallel the results obtained in the present heat of adsorption study. Thus the reinforcing Grade 6 black shows high initial heats of adsorption and the low reinforcing ability of the graphitized Grade 6 black is reflected in considerably lower initial heats. The furnace blacks of intermediate reinforcing ability show intermediate heats. Since the difference in reinforcing ability of the Grade 6 and graphitized Grade 6 (Graphon) cannot be associated solely with differences in particle size or surface area, the present results indicate that the activity or state of the surface of the carbon black plays an important part in reinforcement. While the methods described in this and the previous publication are evidently successful in giving a quantitative comparison of the activity of various carbon black surfaces, we realize that application of these results to the system carbon black and rubber implies that the forces involved are van der Waals in nature. If such an interpretation is accepted and the magnitude of the van der Waals forces is judged from the present heats of adsorption, then a considerable mobility must be assigned to the carbon black particle in a rubber mix. The maximum difference in the heats of adsorption of the $C_4$ and $C_5$ hydrocarbons on reinforcing carbon black gives a value of some 4 kcal. as the binding energy for a —$CH_2$ group to the carbon black surface. This value compares with the 2–3 kcal. associated with the restricted rotation about a *carbon-to-carbon single bond*.[14] Since the elasticity and flexibility of rubber molecules are associated with rotation about the carbon-to-carbon bonds[15] it may be argued that a restricting potential of about the same order should not offer any very serious barrier to the migration of a —$CH_2$ group over the surface of a carbon black particle.[16] These observations are supported by data of Gerke[17] and his co-workers, indicating a marked tendency for the carbon black in an unvulcanized tire stock to undergo considerable flocculation at temperatures of 149 to .188°. Bulgin[18] also has experiments leading to similar conclusions. He found that the d. c. conductivity of a freshly milled carbon black loaded rubber

(14) Kistiakowsky and Rice, *J. Chem. Phys.*, **8**, 618 (1940).

(15) James and Guth, *ibid.*, **11**, 455 (1943).

(16) To account for the mobility of rubber molecules on the carbon black surface, it appears to be unnecessary to postulate the simultaneous desorption of all the adsorbed —$CH_2$ groups of any given rubber molecule. Because the hydrocarbon chains are held together largely by single bonds with nearly free rotation around these bonds, a long chain would be permitted to change its configuration by small steps involving no more than two or three —$CH_2$ groups. Thus the energy required for surface migration may be relatively small.

(17) Gerke, *et al.*, U. S. Patent 2,118,601 (1938).

(18) Bulgin, *Trans. Inst. Rubber Ind.*, **21**, 188 (1945).

stock increased tenfold on standing for fifteen minutes at 100°.

On the other hand, it may be argued that a localized cross-linkage, approaching a chemical bond, is essential to produce the increase in tensile strength, stiffness and abrasion resistance imparted to rubber by carbon black. We felt that some indication of this type of association might be evident when the unsaturated hydrocarbons were used as adsorbates. If such localized linkages are present, they evidently are too few in number to be observed in the present method. This, of course, does not rule out the possibility of localized cross-linkages since only a small per cent. of the carbon black need thus be associated to produce a marked effect in the elastic properties of the rubber. However, if only a small per cent. of the carbon black is presumed to be effective in reinforcement, it is difficult to understand why the properties of the rubber improved steadily with carbon black loadings as high as 30%. Adsorption experiments now in progress under conditions of temperature which should enhance chemisorption if present should shed further light on the question.

Whether the association between carbon black and rubber is of the van der Waals type or more closely approaches chemisorption, or some combination of both, the nature of the carbon surface as described here is doubtless of considerable significance. Since the energy of binding of van der Waals adsorbed molecules is not altered by the presence or absence of surface oxides but is altered by high temperature treatment sufficient to induce graphitization of the black, we are tempted to interpret the high energy sites on the carbon surface as regions of lower order of crystallinity. Warren and Biscoe[4d,e] have described the carbon particle as an essentially spherical aggregation of quasigraphitic crystallites. Some of these crystallites are undoubtedly close to graphite in structure while others show a high degree of randomness with regard to orientation of the graphite platelets about the layer normal. It is this more disordered material which we feel is responsible for the active sites on the carbon surface. At sufficiently high temperatures this material becomes more crystalline and approaches graphite in structure and the more active sites disappear.

## Summary

1. We have measured differential heats of adsorption of a series of saturated and unsaturated hydrocarbons on a number of carbon blacks of varying rubber reinforcing ability.

2. The magnitude of the heats appears to indicate that the adsorption of both saturated and

unsaturated hydrocarbons is essentially of the van der Waals type.

3. The general conclusions to be drawn from this work are remarkably similar to those of a previous investigation using several elementary gases as adsorbates. Specifically the differences in surface activity as shown by the heat measurements with hydrocarbons, as with the elementary gas adsorbates, appear to parallel the rubber reinforcing properties of the blacks which have been investigated.

4. We have found no marked difference between the differential heats of adsorption for the saturated and corresponding unsaturated hydrocarbons. Hence it may be said that the results so far lend no support to the theory that the reinforcing effect of carbon black in rubber is in some way associated with the unsaturated character of the latter. It is hoped that further experimental investigations now being planned may yield further evidence to check this point.

AMHERST, MASS.                    RECEIVED MARCH 26, 1947

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# The Decomposition of Benzoyl Peroxide in Solvents. II. Ethers, Alcohols, Phenols and Amines

BY PAUL D. BARTLETT AND KENZIE NOZAKI[1]

In a previous paper[2] it was shown that in solvents which do not markedly accelerate the decomposition of benzoyl peroxide, this decomposition is of mixed order and can be resolved kinetically into a spontaneous unimolecular reaction and a radical-induced chain reaction which is of higher order. In this paper we report an investigation of the decomposition of benzoyl peroxide in solvents which have a strongly accelerating effect upon the decomposition.

## Experimental Results

**The Decomposition of Benzoyl Peroxide in Ethers.**—Earlier it was found that the decomposition of benzoyl peroxide in dioxane and ethyl ether was much faster than in most other solvents.[2] To test the generality of the rapid reaction, a number of ethers were tried as solvents for the decomposition. The results summarized in Table I indicate that the ethers vary all the way from diethyl ether, in which the reaction is over 60% complete in five minutes, down to anisole and diphenyl ether, which behave as normal aromatic

### TABLE I

THE DECOMPOSITION OF BENZOYL PEROXIDE IN ETHERS AT 79.8°

% Decomposition of a 0.197 $M$ solution

| Ether | 5 min. | 10 min. | 15 min. | 30 min. | 60 min. | 240 min. |
|---|---|---|---|---|---|---|
| Dimethyl | 2.7 | | 11.2 | | | |
| Diethyl | 61.2 | 75.2 | | | | |
| Di-$i$-propyl | 22.3 | | 59.2 | | | |
| Di-$n$-butyl | 31.6 | | 68.9 | | | |
| $t$-Butyl methyl | 10.1 | | 26.8 | | | |
| Divinyl | | | 23.5 | 46.2 | | |
| Dioxane | | | | 67.6 | 82.4 | |
| Anisole | | | | | 14.5 | 47.3 |
| Phenetole | | | | | 59.6 | 93.3 |
| Diphenyl | | | | | 14.7 | 45.7 |

(1) Pittsburgh Plate Glass Fellow, 1943–1946.
(2) Part I: Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946). See also Cass, *ibid.*, **68**, 1976 (1946).

solvents in which the reaction is less than 15% complete in an hour. This is a range of more than 50-fold in rate of reaction under comparable conditions. Ethers containing phenyl and methyl groups appear to be less reactive than the others.

The effect of oxygen was determined since oxygen inhibition is a characteristic of many chain reactions involving free radicals. The results from the decomposition of benzoyl peroxide in $n$-butyl ether, listed in Table II, suggest that oxygen has a marked inhibitory effect. In fact, the iodometric peroxide titer of samples heated in air first decreased and then increased beyond the original value. This must have been due to the formation of new peroxides from the oxygen in the air. Free radicals from the decomposition of benzoyl peroxide were undoubtedly involved in the latter reaction since pure $n$-butyl ether was found to form no peroxide under the experimental conditions. The results listed in the table for the decompositions in air do not give a true indication of the amount of benzoyl peroxide decomposed because of the formation of new peroxides. However, it is evident that very little decomposed since over half of the benzoyl peroxide separated as fine white crystals when a mixture of $n$-butyl ether and benzoyl peroxide was cooled after having been heated in air for thirty minutes at 79.8°.

### TABLE II

THE EFFECT OF OXYGEN ON THE DECOMPOSITION OF BENZOYL PEROXIDE IN $n$-BUTYL ETHER AT 79.8°

| Conditions | % Decomposition of 0.2 $M$ peroxide | | |
| | 5 min. | 15 min. | 30 min. |
|---|---|---|---|
| Vacuum | 31.6 | 68.9 | 87.5 |
| Air | 2.7 | 0.7 | −10.8 |

The decomposition of benzoyl peroxide accelerated by ether was carried out in the presence of vinyl acetate to determine whether free radicals capable of initiating polymerization were formed. Benzoyl peroxide was decomposed in 1:1 mixtures