The products of reduction at the 2- and the 6-positions may absorb less strongly in the 340 mμ region than does the product of reduction at the 4-position. Only the latter product would be expected to show enzymatic activity.[7]

(7) M. E. Pullman, *Federation Proc.*, **12**, 255 (1953).

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Preparation of Highly Compressed Samples for Adsorption Studies[1]

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While determining the B.E.T.[3] surface area of a highly compressed sample of TiO_2, it was discovered that equilibrium time for coverages between $0.5V_m$ and saturation was very much greater than usual, 8–10 hours as compared to 1–2 hours in less compact samples. When the B.E.T. surface area plot was made a non-linear curve was obtained as shown by the dotted curve through the circles with a left bar in Fig. 1. The surface area determined

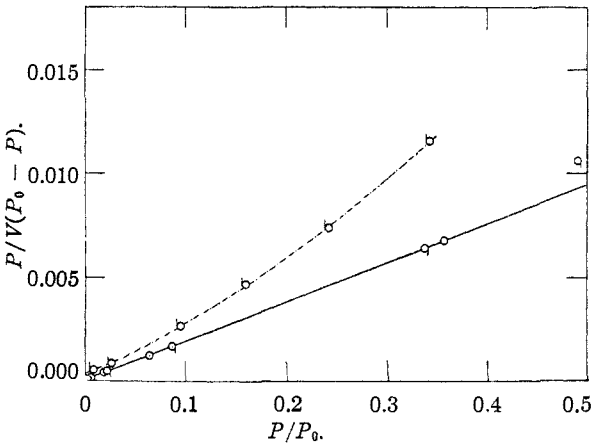

Fig. 1.—B.E.T. plot for nitrogen on TiO_2: o, points for loosely packed test sample; b, points for highly compressed samples; ϙ, points for highly compressed samples after vibration.

by means of a straight line through the low pressure points is 134.5 m.²/g. However, a portion of the same sample had already been run in a small testing chamber, and this sample gave an excellent linear B.E.T. plot as shown by the plain circles in Fig. 1. This test sample was loosely packed relative to the first mentioned sample, and equilibrium was reached in 1–2 hours. The surface area obtained for the test sample is 230.0 m.²/g.

From these results it was concluded that some TiO_2 was not available to the gas in the first sample and that the slow equilibration was caused by gas leaking through solid cakes resulting from high compression. The packed calorimeter was vibrated by means of an ordinary electric vibrating machine. The calorimeter was clamped above the vibrator with a rubber stopper placed between to absorb most of the shock. It was not necessary to use the vibrating mechanism; the vibration of the body of the machine was apparently sufficient to loosen the packing. In order to prevent the machine from getting too hot, the sample was vibrated periodically for about 8 hours.

After the treatment described above the B.E.T. surface area determination was made again with nitrogen. This time, equilibrium was attained in less than 1 hour and in 0.5 hour for some points, all above coverages of $0.5V_m$. The points below $0.5V_m$ were, as usual, slow. The B.E.T. plot obtained for this run is not only linear, but falls on the same plot as for the test sample. These data are shown by the circles with a right bar in Fig. 1.

The authors wish to recommend this technique for preparing highly compressed samples used in adsorption studies at very low temperatures where the dead space corrections are large.

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The Reactions of *p*-Arsanilic Acid and 4-Hydroxyphenylarsonic Acid with Brominated Fatty Acids[1,2]

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In the course of a study of the preparation of homologs and analogs of Tryparsamide, the condensations of a number of brominated fatty acids with *p*-arsanilic acid and 4-hydroxyphenylarsonic acid were attempted. Standard conditions known to give satisfactory results in the preparation of N-4-arsonophenylglycine[3] and several variations from these conditions (including the use of sodium iodide as a catalyst) all failed to bring about the condensation of α-bromobutyric, α-bromoisobutyric, α-bromovaleric and α-bromoisovaleric acids with *p*-arsanilic acid. However, condensations of *p*-arsanilic acid with α-bromopropionic and β-bromopropionic acids were successful under the standard conditions[3] giving N-(4-arsonophenyl)-α-aminopropionic acid (I) and N-(4-arsonophenyl)-β-aminopropionic acid (II). These products did not recrystallize from hot water as readily as the lower homolog, N-4-arsonophenylglycine, making their isolations somewhat more difficult and resulting in lower yields.

Preparation of α-(4-arsonophenoxy)-propionic acid (III) and β-(4-arsonophenoxy)-propionic acid (IV) were carried out following conditions outlined[4] for 4-arsonophenoxyacetic acid but the yield for the β-isomer was very low. Here again recrystallization and purification were more difficult than with the lower homolog.

The ethyl esters of I, II and III were prepared using the method given by Jacobs and Heidelberger[5] for the ethyl and methyl esters of N-4-arsonophenylglycine. The amide of I (a higher

(1) This Research was carried out under Contract N6ONR, Task Order X, of the Office of Naval Research.

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(3) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(1) This work was aided by a grant to the University of Louisville from the Kentucky State Medical Research Commission.

(2) From the M.S. Thesis of Marvin Greenwald, 1952.

(3) German Patent 204,644.

(4) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 75.

(5) W. A. Jacobs and M. Heidelberger, THIS JOURNAL, **41**, 1950 (1919).