[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, JOHNS HOPKINS UNIVERSITY]

The Adsorption of Water Vapor on Carbon Black

BY P. H. EMMETT[1] AND R. B. ANDERSON[2]

Several studies have been reported in the literature relative to the adsorption of water vapor on carbon black.[3] In the present work it has been possible not only to note the change in the water isotherm of carbon blacks on high temperature degassing but also to check the surface areas of the carbon blacks before and after the high temperature heating to make sure that no marked surface area alteration was taking place in the samples as a result of the high temperature treatment. The results are interesting, both as regards the information they give, relative to the properties of carbon black as a function of degassing temperature and also because they illustrate isotherms in which the volume of adsorbate corresponding to a monolayer is reached only at relative pressures in excess of 0.85. The work is part of a project that had to be discontinued because of the urgency of war research.

Experimental and Results

The surface area measurements were made with nitrogen at −195°, by the standard procedure that has been described in a number of previous publications.[4,5] Water adsorption isotherms at room temperatures were determined by two methods—volumetric and gravimetric. In the volumetric method, the conventional adsorption apparatus was used. A standard procedure was adopted by which the adsorbent was momentarily shut off by a stopcock after equilibration, and the pressure of water vapor measured by compressing the vapor in the calibrated measuring buret until the pressure was in the range of 10–15 mm. A similar procedure was used for the inlets of water vapor. Other isotherms were determined gravimetrically, using an oil manometer to determine the equilibrium pressure. The carbon black was contained in a bulb which could be closed with a stopcock and detached from the system by means of a ground glass joint for weighing on an analytical balance. In Figs. 1 and 2, the circles indicate points determined volumetrically and the squares, gravimetrically. Both procedures gave identical isotherms as shown by the water isotherms for Grade 6 Spheron (Fig. 1), which contains points for both volumetric and gravimetric methods. A few desorption points were determined on the water isotherms, these being indicated by solid squares or circles.

The degassing of the carbon black samples was carried out in an apparatus similar to that described by Lowry and Hulett.[6] It was possible to degas the carbon black in a platinum crucible at temperatures up to 1200°, to measure and analyze the evolved gas, and to transfer the sample to the adsorption apparatus without exposing it to air.

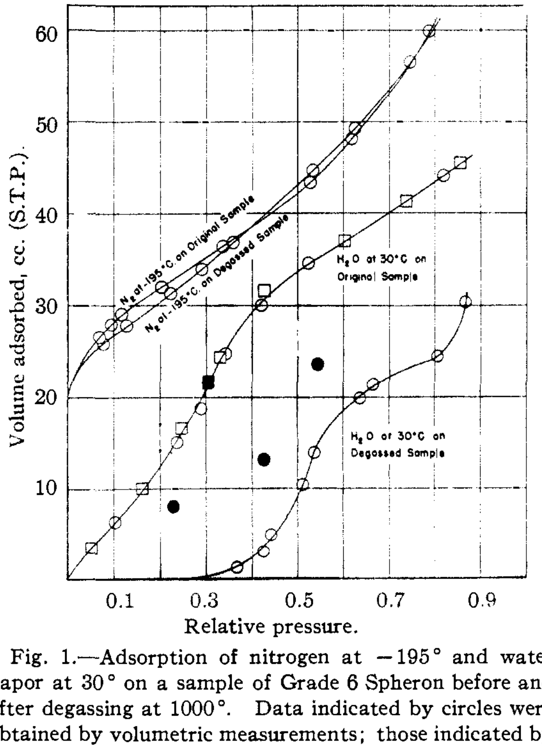

Fig. 1.—Adsorption of nitrogen at −195° and water vapor at 30° on a sample of Grade 6 Spheron before and after degassing at 1000°. Data indicated by circles were obtained by volumetric measurements; those indicated by squares were obtained gravimetrically. Solid circles and squares are desorption points.

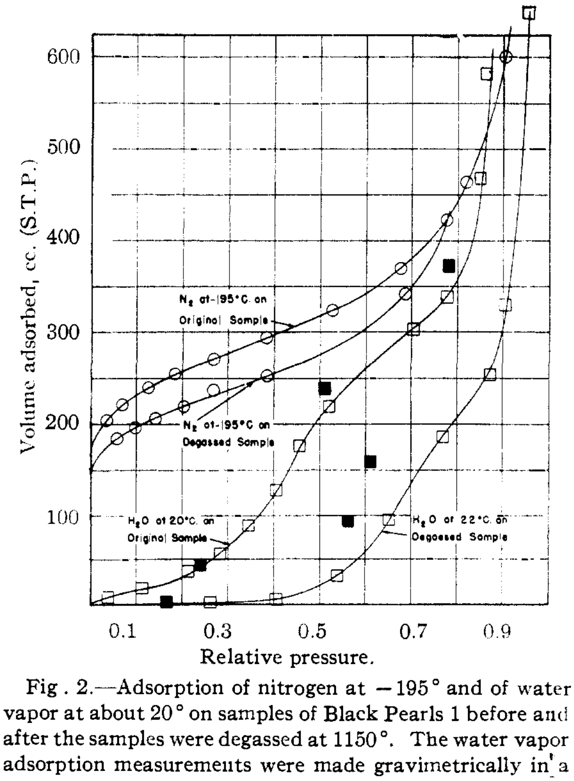

Fig. 2.—Adsorption of nitrogen at −195° and of water vapor at about 20° on samples of Black Pearls 1 before and after the samples were degassed at 1150°. The water vapor adsorption measurements were made gravimetrically in a static system. Solid squares are desorption points.

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[3] Dewey and Lefforge, *Ind. Eng. Chem.*, **24**, 1045 (1932).

[4] Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

[5] Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

[6] Lowry and Hulett, *ibid.*, **42**, 1408 (1920).

The carbon blacks used were Grade 6 Spheron, and Black Pearls 1 (Carbolac 1 in a pelletized or beaded form); both of them were furnished by Godfrey L. Cabot, Inc.[7] Grade 6 Spheron is a Medium Processing Channel Black whereas the Black Pearls 1 is a color black widely utilized in the paint and lacquer industry.

The nitrogen and water vapor adsorption for Grade 6 carbon black before and after degassing to 950–1000° are shown in Figure 1. It is evident that the black showed practically no change in its total surface area nor in the shape of the nitrogen adsorption isotherm. In contrast to this, the change in the appearance of the water isotherm is very striking. The desorption points for the water isotherm on the degassed sample in Fig. 1 are seriously to be questioned because they do not indicate that the desorption curve will rejoin the adsorption at about 0.4. On the other hand, the single desorption point by the more reliable gravimetric procedure on the water isotherm for the original sample falls on the adsorption curve, as it should, at about 0.3 relative pressure.

The nitrogen adsorption isotherms for Black Pearls 1, before and after degassing to 1150–1200° (Fig. 2), show some slight differences, but definitely do not indicate the development or destruction of any porosity as a result of the high temperature evacuation. This agrees with the observations of Smith, Thornhill and Bray[8] on this same kind of carbon black. The water isotherms show much the same differences on the degassed, compared to the original sample as shown for Grade 6 carbon black. For both of these, a monolayer of adsorbed water, as judged by the surface area of the carbon black and a 10.5 sq. Å. cross sectional area of the water molecule is picked up on the degassed sample only when relative pressure is above about 0.85. The desorption points indicate some hysteresis on the water isotherms for both the original and degassed samples.

Discussion

The alteration in the carbon black water adsorption isotherms, brought about by high temperature degassing, as illustrated by the curves in Figs. 1 and 2, has been observed by previous workers. Dewey and Lefforge,[3] for example, found a very similar effect on removing the volatile matter from a carbon black by heating in a restricted supply of air at temperatures up to about 700°. This is the first time, however, that it has been possible to compare the water isotherms on the carbon black with the amount of nitrogen required to form a monolayer and to show, thereby, that the covering of the surface with water vapor is truly very small on a degassed carbon, until fairly high relative pressures are obtained.

Lowry and Hulett,[9] Lowry[10] and Gustaver[11] have suggested the use of water adsorption isotherms for calculating the pore distribution in activated charcoals. The appearance of isotherms *c* and *d* of Figs. 1 and 2 for non-porous degassed carbon black samples seems to us ample reason for concluding that such pore size calculations for water adsorption isotherms on charcoal should be seriously questioned. If the surface of the degassed carbon blacks can yield isotherms for water adsorption that are the same, up to about 0.85 relative pressure, as obtained by activated charcoal, it is evident that one cannot draw conclusions as to the porosity of the charcoal from the adsorption portion of the isotherms.

Although the data on carbon black appear to indicate that adsorption is to be preferred to capillary condensation as an explanation for the shape of the water adsorption isotherm on charcoal, they do not necessarily preclude the possibility that capillary condensation is involved in charcoal after the samples have been exposed to sufficiently high relative pressure of water vapor. Indeed, it is difficult to imagine an explanation for the hysteresis that is observed in the desorption of water vapor from charcoal without assuming the existence of capillary condensation at sufficiently high relative pressures. Of course, if further work confirms the reality of hysteresis in the desorption of water vapor from degassed carbon blacks having particles as large as those of Grade 6 carbon, the case for interpreting water isotherms on charcoal as due to adsorption[12] rather than capillary condensation will be greatly strengthened.

The water adsorption isotherms on both the degassed carbon blacks are indicative of heats of adsorption at relative pressures below about 0.5 that are lower than the heat of liquefaction. The isotherms on the degassed carbons between about 0.5 and 0.85 relative pressures are similar to those obtained on charcoals that have been shown to be characterized by heats of adsorption that increase as the relative pressure increases.[13] The water isotherms made on the blacks prior to the high temperatures are clearly indicative of heats of adsorption that are larger than for the degassed samples but still only about equal to the heat of liquefaction. The greater water adsorption on the original samples is doubtlessly to be associated with the existence of the carbon–oxygen complex that is known to be present as volatile matter.

Monolayers of adsorbed water vapor do not appear to form on the carbon blacks below relative pressures of about 0.85 or 0.9; the multilayer formation on the degassed carbolac appears at a relative pressure larger by about 0.1 unit than that at which it appears on the sample that has not been degassed. A detailed analysis of the water isotherms will be postponed until data are obtained at other temperatures.

Summary

Evacuating two typical carbon blacks at 1000 to 1200° so altered the nature of their surfaces as to yield water adsorption isotherms resembling those found for steam activated charcoal. However, nitrogen adsorption isotherms before and

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(7) The authors wish to acknowledge gratefully the help given by Godfrey L. Cabot, Inc., in the form of fellowship funds to defray the cost of this work.

(8) Smith, Thornhill and Bray, *Ind. Eng. Chem.*, **33**, 1305 (1941).

(9) Lowry and Hulett, THIS JOURNAL, **42**, 1393 (1920).

(10) Lowry, *ibid.*, **46**, 824 (1924).

(11) Gustaver, *Kolloidchem. Beihefte*, **15**, 184 (1922).

(12) McBain, Porter and Sessions, THIS JOURNAL, **55**, 2294 (1933).

(13) Coolidge, *ibid.*, **48**, 1795 (1926); Lamb and Coolidge, *ibid.*, **42**, 1146 (1920).

after this evacuation show that the samples did not develop porosity and did not increase their surface areas during degassing.

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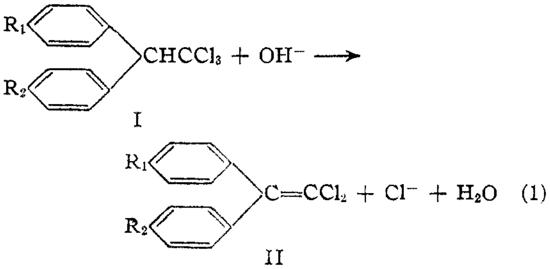
A Kinetic Study of the Dehydrochlorination of Substituted 2,2-Diphenylchloroethanes Related to DDT[1]

BY STANLEY J. CRISTOL

Brand and Busse-Sundermann[2] have reported a semiquantitative kinetic study of the dehydrochlorination of several 2,2-diaryltrichloroethanes with potassium hydroxide in 96% ethanol at the boiling point of the solution. The reaction studied is represented by equation (1).



These workers, as well as Neal[3] and Gunther,[4] have demonstrated the quantitative nature of this reaction, and their work has indicated that only one mole of chloride ion is produced per mole of trichloroethane at 80°. Grummitt, Buck and Jenkins[5] have shown that at elevated temperatures hydrolysis of the ethylene (II, $R_1 = R_2 =$ Cl) may occur with the formation of a substituted diphenylacetic acid.

In connection with an extended study in our laboratory of the insecticide DDT (I, $R_1 = R_2 =$ Cl) and of analogs of DDT, a quantitative study of the effect of modifications in molecular structure upon chemical reactivity was undertaken. Alkaline dehydrochlorination was chosen as a suitable reaction, as its course may be conveniently followed by titration for chloride ion and the reaction forms the basis for an analytical method for the determination of DDT.[3,4] This reaction was also of interest in connection with work on the mode of action of DDT, since at least two groups of workers[6,7] have suggested the possibility that dehydrochlorination may be involved in the toxic action of DDT against insects.

The purpose of this paper is to report kinetic data on the elimination of hydrogen chloride with ethanolic sodium hydroxide from compounds of type I with $R_1 =$ H and $R_2 =$ H or Cl, and with $R_1 = R_2 =$ H, Cl, Br, F, CH_3, CH_3O or *t*-butyl, and of one series of related compounds in which the trichloromethyl group has been replaced with dichloro- and monochloromethyl groups. This work also includes data on the *o,p'*-DDT isomer, 1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane. Rate constants were obtained at 20.11 and 30.37° in 92.6 weight per cent. ethanol with all the compounds studied. The effect of change of solvent to 87.0 and 76.0 weight per cent. ethanol on the rate of dehydrochlorination of *p,p'*-DDT has also been studied.

Measurement of Reaction Rates.—The following procedure was used to follow the rates of reaction of the various chloroethanes with sodium hydroxide: A solution containing the ethane, 0.005 to 0.01 *M*, and sodium hydroxide, 0.01 to 0.05 *M*, was prepared at the desired reaction temperature by dissolving the required weight of the ethane in "190-proof" ethanol in a volumetric flask (adding the required amount of water in certain cases), equilibrating the solution in a thermostat, and then adding, by means of a pipet, a measured volume of standard ethanolic sodium hydroxide. The solution was then made up to volume, mixed well by shaking, and replaced in the thermostat at 20.11 or 30.37°. Temperature control was constant within ±0.03°. During the course of a run six or seven 10.00- or 20.00-ml. aliquot samples were transferred to an Erlenmeyer flask at bath temperature, and the reaction was then stopped by the addition of about 25 ml. of 1.5 *N* nitric acid. The solutions were then treated with 5.00 ml. of standard 0.03 *N* silver nitrate solution, and the precipitate was coagulated with nitrobenzene. The excess silver ion was titrated with standard 0.02 *N* ammonium thiocyanate with the use of a microburet and ferric sulfate as indicator in the customary Volhard procedure.

In extremely rapid reactions the temperature of the room was maintained within 1° of the bath temperature to minimize errors arising during the period of transfer, which was approximately one minute.

Sodium hydroxide was chosen as the basic re-

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[1] This research was conducted under a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine. Not copyrighted.

[2] Brand and Busse-Sundermann, *Ber.*, **75**, 1819 (1942).

[3] Neal and co-workers, *U. S. Pub. Health Service*, Suppl. to Pub. Health Repts. No. 177 (1944).

[4] Gunther, *Ind. Eng. Chem., Anal. Ed.*, **17**, 149 (1945).

[5] Grummitt, Buck and Jenkins, THIS JOURNAL, **67**, 156 (1945).

[6] Fleck and Haller, *ibid.*, **66**, 2095 (1944).

[7] Martin and Wain, *Nature*, **154**, 512 (1944).