Summary

The dissociation pressures of the following systems have been measured over a range of temperatures: dilituric acid ($3 \rightleftarrows 1\ H_2O$) and ($1 \rightleftarrows 0\ H_2O$), *d*-galactose ($1 \rightleftarrows 0\ H_2O$), creatine ($1 \rightleftarrows 0\ H_2O$). For the organic monohydrates both the $\Delta H°$ and the $\Delta S°$ of dissociation appear to be unusually low as compared with typical values for inorganic systems.

WASHINGTON, D. C. RECEIVED MAY 26, 1948

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Reaction between Atomic Hydrogen and Molecular Oxygen at Low Pressures. Surface Effects[1]

BY ELMER J. BADIN

When atomic hydrogen produced by electrical discharge and molecular oxygen are allowed to react, hydrogen peroxide and water are formed. Bonhoeffer and Boehm[2] first observed that, at liquid air temperatures, large quantities of hydrogen peroxide resulted. Subsequently Geib and Harteck[3,4] showed that peroxide formation under these conditions must form by a wall reaction since it is eliminated at temperatures above −79°.

In this paper additional data of a somewhat more quantitative nature are presented for the low temperature reaction. Particular attention has been paid to water formation in order to arrive at a more satisfactory mechanism for its formation than previously proposed.

In addition, the question of whether the decrease of condensable products (peroxide and water) with increase of temperature is due solely to hydrogen atom recombination or recombination of hydroxyl or HO_2 has been considered. The study of the reaction has, therefore, been extended to a higher temperature than heretofore and the effect of surface treatment (phosphoric acid, Pyrex and potassium chloride) determined in this higher temperature region. It was expected that the effects of a potassium chloride surface (shown[5] to cause OH recombination and not H recombination) and the other surfaces would supply additional information in regard to the recombination reactions occurring.

Experimental

The trap arrangement and metering system are shown in Fig. 1. A discharge tube, G, of total length about 2.5 meters, with hollow cylindrical aluminum electrodes, F and F′, was used for dissociating the hydrogen. The tube was coated with phosphoric acid. A 15-kilovolt transformer with 110 volts a.c. primary supplied the dissociating potential. The hydrogen atom concentration, assuming all hydrogen in the products as originally in the atomic form and based on products formed in the low-temperature experiments, was estimated to be of the order of 70%.

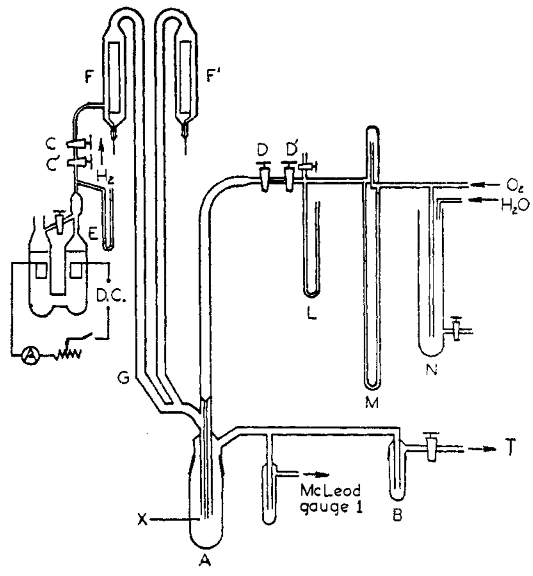

Fig. 1.—Apparatus: T, trap, McLeod gage 2, Langmuir pump, Megavac pump.

Hydrogen was introduced without drying from an electrolysis U-tube E containing dilute sulfuric acid. The gas was admitted through stopcocks C and C′ leading into one end of the discharge tube. The amount of hydrogen was determined by the quantity of electricity used. Oxygen was admitted through throttling stopcocks D and D′ from a capillary-type flowmeter M in series with a static manometer L. The oxygen flowmeter was carefully calibrated in the desired range and the flow maintained constant by an adjustable water column N. For experiments with hydrogen and oxygen both admitted to the discharge tube, a double electrolyzer was used and the premixed gases admitted. Pressures were read on McLeod gage 1 adjacent to the reaction trap A. Pressures recorded were without the discharge operating. Since pressures were measured on the exit side of the reaction trap, pressures in the discharge tube were somewhat higher.

The concentric reaction tubes X leading into trap A (51 mm. O.D.) were of 17.5 mm. and 8.0 mm. O.D., respectively. Trap B was connected to trap A by 17.5 mm. O.D. untreated Pyrex tubing. Two positions for trap B were used; the first about 100 cm. from the point of mix-

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[1] The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and with Contract N6-ori-105 with the Bureau of Aeronautics and Office of Naval Research, as coördinated by Princeton University. Acknowledgment is due Dean Hugh S. Taylor, who has general supervision of this project, and Professor Robert N. Pease.

[2] K. F. Bonhoeffer and E. Boehm, *Z. physik. Chem.*, **119**, 385 (1926).

[3] K. H. Geib and P. Harteck, *Ber.*, **65**, 1551 (1932).

[4] K. H. Geib and P. Harteck, *Z. physik. Chem.*, **170**, 1 (1934).

[5] H. S. Taylor and G. I. Lavin, THIS JOURNAL, **52**, 1910 (1930); see also A. A. Frost and O. Oldenberg, *J. Chem. Phys.*, **4**, 642 (1936); W. V. Smith, *ibid.*, **11**, 110 (1943).

ing, the second about 30 cm. from the point of mixing. When peroxide and water formed, they condensed as an ice on the reaction trap walls. The trap was warmed to room temperature and weighed. Peroxide was determined by titration with 0.1 *N* potassium permanganate in the presence of sulfuric acid; water was determined by difference. When water formation alone occurred, it was carefully washed out with anhydrous methanol. An aliquot portion was then titrated electrometrically with Karl Fischer reagent using the method of Wernimont and Hopkinson.[6]

Results and Discussion

The Low-Temperature Reaction.—In Table I data are shown for peroxide and water formation at liquid nitrogen temperature. In the first series of experiments moist hydrogen was streamed through the discharge tube and reacted with molecular oxygen. The products were condensed immediately in the main reaction trap. The peroxide and water formed increase at first and, with further increase in the amount of oxygen, decrease sharply. In each case, however, peroxide and water are formed in the molar ratio of about 1:1. Similar results are obtained when both hydrogen and oxygen are passed through the discharge tube and the products immediately condensed. In this case, however, a much smaller amount of oxygen is necessary to cause a decrease in peroxide and water formed.

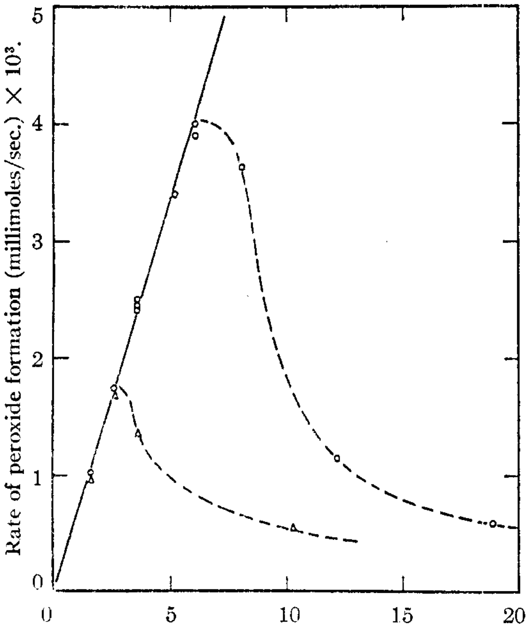

Fig. 2.—Dependence of peroxide formation on oxygen at temperature −196°: O, atomic hydrogen and molecular oxygen; △, hydrogen and oxygen through discharge.

The mechanism proposed for peroxide formation by Geib and Harteck[4] is

$$H + O_2 + M \xrightarrow{k_1} HO_2 + M \qquad (1)$$

$$HO_2 + H + M \xrightarrow{k_2} H_2O_2 + M \qquad (2)$$

where the third body is the wall. For a steady-state concentration of HO_2, one arrives at the simple expression

$$d[H_2O_2]/dt = k_1[O_2][H][M] \qquad (3)$$

This indicates that, with an excess of atomic hydrogen and constant condition of the wall as in these experiments, the rate of peroxide formation should be proportional to the oxygen concentration. This is shown to be true (Table I) at low oxygen concentrations (the rates of peroxide formation and water formation have been divided by the amount of oxygen introduced per second). This is further illustrated for peroxide formation only by Fig. 2. A similar result follows for water formation. When the oxygen is increased above a certain value a sharp decrease in peroxide results as shown by the dotted line. This must be due primarily to the gas phase recombination reaction

$$H + H + O_2 \longrightarrow H_2 + O_2 \qquad (4)$$

When both hydrogen and oxygen are present in the discharge, recombination reactions occur at much lower oxygen concentrations. The recombination reaction might also involve OH.

TABLE I

PEROXIDE AND WATER FORMATION FROM ATOMIC HYDROGEN AND MOLECULAR OXYGEN

Temperature −196°

Gases introduced			Products			
			H_2O_2		H_2O	
Pressure[a] $H_2 + O_2$, mm.	H_2, (millimoles/sec.) × 10^3	O_2 (millimoles/sec.) × 10^3	Rate (millimoles/sec.) × 10^4	Rate/O_2 rate	Rate (millimoles/sec.) × 10^3	Rate/O_2 rate
Hydrogen through discharge tube						
0.27	12	3.6	2.46	0.68	2.2	0.61
.27	12	3.6	2.42	.67	2.1	.59
.27	12	3.6	2.50	.69	2.3	.64
.27	12	3.6	2.45	.68	2.1	.57
.27	14	1.6	1.08	.68	1.1	.69
.27	13	2.6	1.74	.67	1.8	.68
.27	12	3.6	2.50	.69	2.4	.68
.27	10	5.2	3.40	.65	3.1	.60
.36	12	6.1	3.96	.65	3.1	.51
.42	12	8.1	3.63	.45	3.5	.43
.50	12	12	1.15	.09	1.2	.10
.58	12	19	0.59	.03	0.6	.03
.19	12	0	0.11	..	...	..
Hydrogen–oxygen through discharge tube						
0.27	14	1.6	0.98	0.61	1.1	0.71
.27	13	2.6	1.68	.65	1.4	.55
.27	12	3.6	1.35	.38	1.1	.31
.27	10	5.2	0.55	.11	0.6	.12

[a] Measured on exit side of reaction trap, without discharge, at room temperature.

Although reactions (1) and (2) adequately account for peroxide formation, water formation, which parallels peroxide formation at −196°, must also occur at these low temperatures by a re-

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[6] G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 272 (1934).

action having no activation energy. Water formation is readily accounted for if it is assumed that hydrogen peroxide is the primary product and is first formed in an unstable form. The steps occurring are then

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (5)$$

$$HO_2 + H + M \longrightarrow [HO{-}OH]^* + M \qquad (6)$$

$$[HO{-}OH]^* \xrightarrow{\text{cold surface}} H_2O_2 \qquad (7)$$

$$[HO{-}OH]^* \xrightarrow{\text{unstabilized}} OH + OH \qquad (8)$$

Step (6) proposes formation of an unstable intermediate complex of two loosely bound OH radicals. Reactions (5) and (6) are highly exothermic. Failure to dissipate the heat of reaction on a cold surface at the low pressures used here leads to no peroxide in the products. The net result of reactions (5) to (8) in absence of a cold surface is the formation of hydroxyl. Water then can form by

$$H + OH \longrightarrow H_2O \qquad (9)$$

This reaction is exothermic by 118 kcal.[7] and would undoubtedly have no activation energy.

The results obtained by Rodebush, Keizer, McKee and Quagliano[8] for the discharge through water vapor, where only H and OH are present, are strikingly similar to those obtained here. These authors assume the reactions

$$H + OH \longrightarrow H_2O \qquad (10)$$

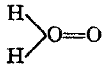
$$OH + OH \longrightarrow H_2O_2 \qquad (11)$$

which yield peroxide and water in the molar ratio of about 1:1 (greater than 60% hydrogen peroxide by weight) at liquid air temperature. They further propose that hydroxyls disappear in the exhaust tubing by a homogeneous mechanism

$$OH + OH \longrightarrow H_2 + O_2 + \sim 20 \text{ kcal.} \qquad (12)$$

Egerton and Minkoff,[9] to account for anomalies in peroxide formation in the thermal reaction between hydrogen and oxygen at higher pressures, have proposed an unstable intermediate similar to that in reaction (6). They consider this as an unstable molecule in which energy is distributed among the vibrational and rotational degrees of freedom for a short time. This results in possible dissociation into two hydroxyls if failure to stabilize the complex on a cold wall or by three-body collisions in the gas phase occurs. The observations of these authors show that some complex such as proposed must exist.

Mention should be made of the isomeric form of hydrogen peroxide suggested by Geib and Harteck.[3] They observed that warming the products, condensed as a solid glassy material, to −80° led to foaming and gas evolution. On the basis of their analyses they concluded that the gas evolved was oxygen and assigned the structure



to the peroxide. They also inferred that this isomer, mixed with the normal form, HO–OH, decomposed on warming according to the reaction

$$H_2O_2 \longrightarrow H_2O + O \qquad (13)$$

The extent of the decomposition observed by them was as high as 41%. The occurrence of this endothermic reaction at low temperature seems very unlikely. In experiments shown (Table I) it has been possible in some cases to account practically quantitatively for all the oxygen introduced. It is concluded that the peroxide is probably of the normal form. The foaming, also observed in these experiments, is probably due to small amounts of dissolved or occluded gases (hydrogen as well as small amounts of oxygen) as was suggested in a remark by Willey.[10] It seems that there is insufficient evidence to assign a structure other than the normal one to the peroxide formed.

If hydrogen peroxide is the primary product, it might be expected that an increase in temperature above −196° would lead to an increase in water at the expense of a decrease in peroxide. This has been found to be true. Geib and Harteck[4] have stated that the amount of water formed between liquid air and carbon dioxide–acetone temperatures is essentially constant. This is true for the actual amount condensed when experiments at −196 and −79° are compared. However, it was found that at −79° incomplete condensation occurred. At temperatures slightly above −196° (*e. g.*, −183°) water formation increases accompanied by a decrease in peroxide. At a still higher temperature (−79°) this decreases to essentially the same amount as is formed at −196° (although peroxide is absent). This is, as stated above, probably due in part to incomplete condensation at the high pumping speeds used. It might also conceivably be due to a change in the nature of the surface leading to recombination reactions. However, in all the low temperature experiments the surface is uniformly wet. This would exclude any pronounced surface effect on the reaction at low temperatures. This is also indicated by observing that peroxide formation at −196° is exactly linear with time and that a phosphoric acid surface at −196° did not change the amount of peroxide formed.

The low temperature experiments, on the whole, indicate the importance of OH for both peroxide and water formation with peroxide as the primary product.

Surface Effects at Higher Temperatures.—In Figures 3 and 4 the effect of surface treatment on peroxide and water formation is shown. The experiments were carried out by mixing the gases from the discharge tube with molecular oxygen in the main reaction trap and condensing

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(7) R. J. Dwyer and O. Oldenberg, *J. Chem. Phys.*, **12**, 351 (1944).

(8) W. H. Rodebush, C. R. Keizer, F. S. McKee and J. V. Quagliano, THIS JOURNAL, **69**, 538 (1947).

(9) A. C. Egerton and G. J. Minkoff, *Proc. Roy. Soc. (London)*, **191**, 145 (1947).

(10) E. J. B. Willey, see P. Harteck, *Trans. Faraday Soc.*, **30**, 141 (1934).

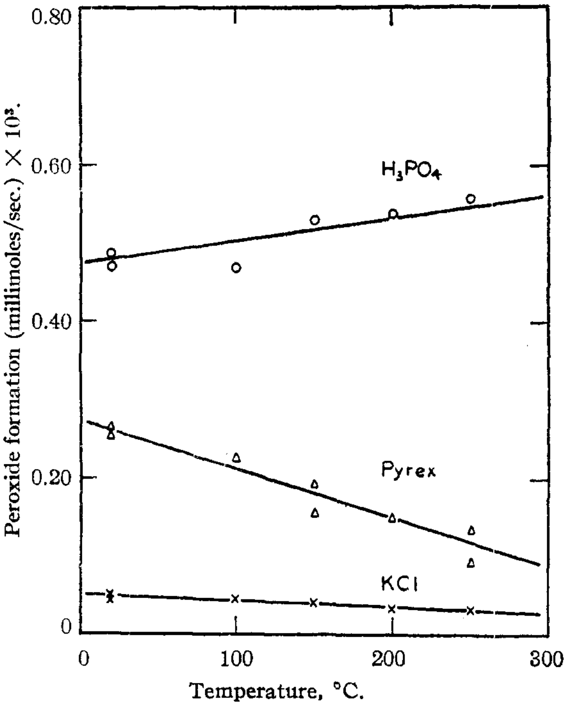

Fig. 3.—Effect of surface on peroxide formation: condensed (−196°), 30 cm. from point of mixing of gases (gases introduced: hydrogen 12 × 10^{-3} millimole/sec.; oxygen, 3.6 × 10^{-3} millimole/sec.; p = 0.27 mm.).

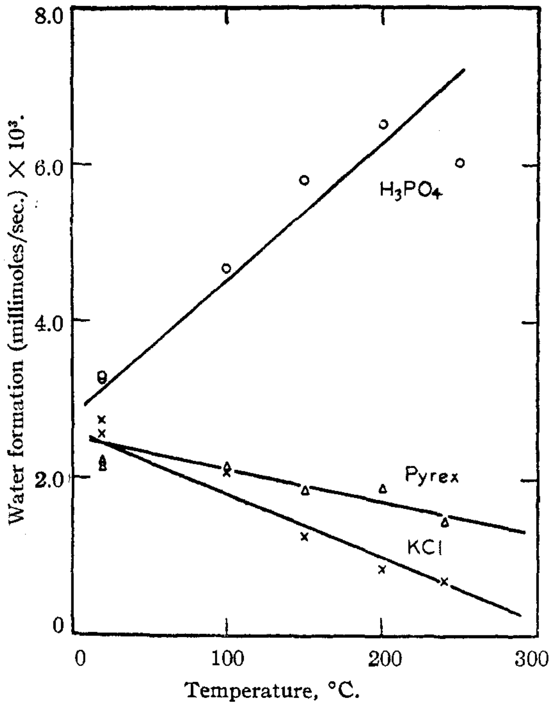

Fig. 4.—Effect of surface on water formation: condensed (−196°), 30 cm. from point of mixing of gases (gases introduced: 12 × 10^{-3} millimole/sec.; oxygen, 3.6 × 10^{-3} millimole/sec.; p = 0.27 mm.).

the products at a given distance from the point of mixing. In each case the surface of the mixing trap was prepared by cleaning the trap and inlet tubes with hot nitric acid and rinsing thoroughly with distilled water. The trap was then either left in this condition for the pyrex experiments or coated with about one normal solution of potassium chloride or phosphoric acid. Drying was initially carried out by evacuation to 10^{-4}–10^{-5} mm. for eighteen hours at room temperature followed by two hours at 150°. Between consecutive experiments the apparatus was evacuated at room temperature for twelve to eighteen hours.

Comparison of the first experiment of Table I with the data of Figs. 3 and 4 shows that, all other conditions being equal, removal of the condensing trap to a position 30 centimeters away from the point of mixing at 20° results in a loss of peroxide of about 90% with only about an 8% loss in water. Further experiments showed that removal of the trap to a position 100 cm. away resulted in only a trace of peroxide and reduced the water by only a very small amount. This indicates that, assuming peroxide is the primary product, OH recombination to yield gaseous products must be occurring.

For peroxide formation (Fig. 3) large differences are noted at 20°. For water formation (Fig. 4) the amount of water formed at 20° was about equal in all three cases. This latter result would seem to be true within the experimental error. An increase in temperature leads to comparable results for both water and peroxide formation. The results obtained suggest that the differences are due mainly to the amount of water present on the surface. Potassium chloride provides a dry surface, pyrex an intermediate wet surface and phosphoric acid a very wet surface which maintains its moisture even at the high temperatures. It is also possible that a reaction between H and OH and water present on the surface is responsible for the action of water in preventing recombination reactions.

The actual steps leading to peroxide and water formation under these conditions are probably similar to those discussed for the low-temperature region. For water formation the additional reaction, $HO_2 + H_2$, having an activation energy of about 5–7 kcal., is possible according to Geib[11] who reports up to 1.5 H_2O per H atom at low atom concentrations and at 20°. However, at the high atom concentrations and low pressures here this would be suppressed. At any rate, H, OH and possibly HO_2 are present and capable of being destroyed at the wall and leading to the results shown. Since hydrogen atom recombination is relatively unaffected by the surfaces used here, the surface effect must be due primarily to a destruction of OH for which a potassium chloride surface is especially suited.

The potassium chloride surface effect on the hydrogen–oxygen reaction is well known. Pease and

[11] K. H. Geib, *Ergeb. exakt. Naturw.*, **15**, 44 (1936).

Chesebro[12] first showed its importance in oxidation reactions. Taylor and Lavin[5] and others[5] found that potassium chloride would not recombine hydrogen atoms but would cause recombination of hydroxyl radicals. Pease[13] also showed that potassium chloride surfaces decreased the rate greatly and eliminated peroxide in the hydrogen–oxygen reaction. Frost and Alyea[14] observed a higher explosion limit at a given temperature for the hydrogen–oxygen reaction when a potassium chloride-coated container was used. The effect of different salt-coated surfaces has also been shown by von Elbe and Lewis.[15] In addition to these observations, many others of a similar nature have been made. All of these results indicate that the specific action of potassium chloride or other salt is that of a dry surface. In the present experiments it was found that surfaces of lithium, sodium and potassium chlorides prepared in the same way gave essentially identical result. In addition, a fresh Pyrex surface resulted in approximately halving both the peroxide and water formed (results in Figs. 3 and 4 were obtained with an essentially wet Pyrex surface).

An interesting observation was made in regard to the effect of oxygen on the chemiluminescence occurring on some of the surfaces. With a clean Pyrex surface a very faint green-blue luminescence occurred on the surface of the main reaction trap at temperatures of 150° and higher. With a potassium chloride coated surface the luminescence was much more pronounced. No surface luminescence was observed with phosphoric acid as the coating. When the oxygen flow was cut off, the luminescence disappeared completely for the Pyrex surface and was many times less intense for the potassium chloride surface. The reaction accompanying luminescence cannot be a reaction leading to water or peroxide since the luminescence was strongest when the peroxide and water were formed in least quantity.

Summary

1. In the low-temperature reaction (−196°) between atomic hydrogen produced by electrical discharge and molecular oxygen the rate of peroxide and water formation is proportional to the oxygen concentration at low oxygen concentrations.

2. At temperatures slightly above −196° water formation increases at the expense of a decrease in peroxide formation.

3. A mechanism involving initial formation of the unstable intermediate complex [HO-OH]* is proposed to account for both water and peroxide formation.

4. Hydrogen and oxygen both present in the discharge lead to similar results.

5. The effect of Pyrex, phosphoric acid and potassium chloride surfaces at higher temperatures has been studied. The effects have been attributed to the relative amounts of water present on the three surfaces. Surfaces of lithium, sodium and potassium chloride gave essentially similar results.

6. This effect of the surface in leading to a decrease in peroxide and water has been attributed to destruction of OH (or possibly HO_2) in addition to H recombination to give molecular hydrogen and oxygen.

7. The chemiluminescence occurring on the chloride coated surfaces is dependent on oxygen and is strongest when peroxide and water are formed in least amounts.

PRINCETON, N. J. RECEIVED MAY 10, 1948

(12) R. N. Pease and P. R. Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928).

(13) R. N. Pease, THIS JOURNAL, **52**, 5106 (1930).

(14) A. A. Frost and H. N. Alyea, *ibid.*, **55**, 3227 (1933).

(15) G. von Elbe and B. Lewis, *J. Chem. Phys.*, **10**, 366 (1942).

[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Studies on Carbon Black. II. Grignard Analysis[1]

BY D. S. VILLARS[2]

Introduction

Analysis by means of Grignard reagent, developed by Kohler, Stone and Fuson,[3] has found extensive application in problems of organic chemistry. It was suggested by Dr. R. H. Gerke that this technique might be of value if applied to a study of oxygen on carbon black. In the present paper a report is given of the results of such a study.

It is well-known that commercial carbon blacks contain varying amounts of volatilizable matter. Some of this is loosely bound, being held by van der Waals (unactivated) adsorption and comes off on heating to 110°. The remainder is tightly bound, being held by activated adsorption and requires heating to around 1000° for liberation. This tightly bound portion of the volatilizable matter is conventionally called "volatile matter" in the carbon black and rubber industry. The present discussion concerns only the latter, chemically adsorbed material. About two-thirds of the tightly bound volatilizable matter is oxygen, the bulk of the remainder being attributable to

(1) For Part I, see THIS JOURNAL, **69**, 214–217 (1947).

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(3) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927); **52**, 3736 (1930).