and perhaps one or more of the reagents, so as to make possible a fast reaction in the body of the solution. This reaction, as evidenced by the red color, reaches a peak in a few seconds, at which point the indophenol produced is adsorbed by the charcoal, and begins to undergo degradation by reacting with the excess reagents under the catalytic influence of the charcoal. A second reaction on the charcoal surface now becomes dominant and the indophenol produced is adsorbed quickly. This second reaction, sensitive to hydrogen-ion concentration, produces the second rise in the curve. However, as the indophenol accumulates, the rate of destruction increases and the curve drops again.

We have, as yet, no explanation which we feel we can offer for the constancy of the final indophenol yield in all the above reactions. It is interesting to note that this value remains constant for at least twenty-four hours in every case.

Experimental

The charcoal used in this investigation was prepared from reagent-grade sucrose. It was carbonized in porcelain casseroles and activated at red heat in silica crucibles for fifteen minutes. The ash content was found to be less than 0.02%. Constant temperature baths maintained the system at 30 or 40 ± 0.03 or 20 ± 0.4°. In general, the method described in the previous paper[1] was used for determining the catalytic activity of the charcoal. It was noted that the filtrate was not appreciably colored upon filtration, but, rather, that the indophenol color appeared only after a few minutes. Although a mild vacuum was used to provide an increased filtering speed, we attribute most of the filtrate yield to a reaction between excess reagents after and during filtration. Another modification of the original procedure consisted in using 36 cc. (six 6-cc. portions) of toluene to extract the charcoal.

In the oxidase experiments we simply omitted the hydrogen peroxide. All buffers were of the citrate type, checked by means of a glass electrode.

In the reactions involving inhibitors either 2.0 cc. of a 2% solution of amyl alcohol in water, or 0.7 cc. of a 2% aqueous solution of potassium cyanide was added one-half minute after the start of the reaction. For curves 4 and 5 in Fig. 2, only the concentrations of the α-naphthol and *p*-phenylenediamine were altered.

A concordance of results of 4 to 5% was consistently obtained, and each point on the curves represents the average of at least three determinations. Near the region of each maximum in the curves the time was varied slightly so as to fix the point of greatest yield.

Summary

1. The peroxidase activity of charcoal in catalyzing the formation of indophenol has been reinvestigated.
2. It now appears that the observed destruction of indophenol after one-half minute is due to a reaction involving excess reagents and catalyzed by charcoal.
3. The oxidase activity of charcoal in the indophenol reaction has been investigated. This action is very similar to the peroxidase action. It is suggested that the formation of indophenol takes place both in solution and on the surface of the charcoal.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, ST. PETER'S COLLEGE]

The Catalytic Properties of Charcoal. III. A Comparison of the Oxidative Properties of Various Charcoals. The Effect of Charcoal Hydrosols on Hydrogen Peroxide and Oxygen

BY JOSEPH F. KEEGEL, WILLIAM A. SURUDA AND CLAUDE SCHWOB

1. A Comparison of the Properties of Various Charcoals.—This Laboratory has been investigating the properties of charcoal for several years.[1] We have used mainly purified animal charcoal and sucrose charcoal. The findings of several investigators[2] have suggested the possibility that other charcoals might be more suitable as catalysts. Moreover, it is one of the aims of this series of investigations to attempt a standardization in the use of charcoal as a catalyst, a need which we believe pressing since, in so far as we have noticed, no two investigators have used exactly the same charcoal.

Hence, in this phase of the investigation we endeavored to find conditions under which charcoals of various kinds may be prepared in a manner easily duplicated without special equipment. Next, we tested these charcoals for catalytic activity in decomposing hydrogen peroxide (cata-

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[1] I, (a) Schwob, THIS JOURNAL, **58**, 1115 (1936); II, (b) O'Brien, Tkac and Schwob, *ibid.*, **60**, 2480 (1938).

[2] (a) Rideal and Wright, *J. Chem. Soc.*, 1813 (1926); (b) Zylbertal, *Biochem. Z.*, **236**, 131 (1931).

lase action), in promoting oxidations with hydrogen peroxide (peroxidase action) and with oxygen (oxidase action). For purposes of comparison, the same charcoals were tested in standard adsorption experiments.

Because we wished that the preparation of our charcoals be simple, a temperature of only 590 to 600° was chosen for activation. While this is a rather low and certainly not optimum temperature,[3] it gave some excellent charcoals.

Four kinds of charcoal were prepared as suggested by the work of Rideal and Wright.[2a] These were made (a) from pure sucrose (yielding a charcoal designated as "C–C" charcoal), (b) from a sucrose–urea mixture (C–N charcoal), (c) from a sucrose–ferric chloride mixture (C–Fe charcoal), and (d) from sucrose with the addition of both the iron salt and urea (Fe–C–N charcoal).

Catalase activity was determined by measuring the rate of evolution of oxygen from an 0.25 molar solution of hydrogen peroxide in the presence of 100 mg. of charcoal. The specific reaction rate was calculated from the data by assuming a unimolecular reaction.

The oxidase activity was determined according to the method of O'Brien, Tkac and Schwob,[1b] the results reported being the final constant yield of indophenol.[4] The peroxidase activity, reported similarly, was also obtained by methods developed in this Laboratory.[1a,b]

In the adsorption experiments two substrates were employed, benzoic acid and acetic acid. The former was used in the method of Miller,[5] and the latter was used in determining the familiar Freundlich adsorption isotherm. Table I summarizes our results.

TABLE I

Charcoal	Miller test, %	Isotherm[a] K	n	Catal. $K \times 10^4$	Oxid. mg.	Peroxid. mg.
C–C	8.17	0.17	0.48	9.0	0.063	0.15
C–N	5.96	.076	.51	23	.12	0.45
C–Fe	16.9	.41	.39	21	.69	1.35
Fe–C–N	10.9	.11	.60	170	.72	3.4

[a] In $x/m = Kc^n$, where c = molar concentration at equilibrium.

A second set of charcoals was then prepared in order to test the reproducibility of the charcoals. Tests showed agreement within 4 to 9% for most of the properties with the notable exception of the catalase activities of the C–N and C–Fe charcoals, which were approximately 25% greater for the second batch, and the peroxidase activity of the C–Fe charcoal which was 15% higher than that of the original batch. However, these deviations were not large enough to disturb the relations between the various properties.

It is evident from Table I that the C–Fe charcoal is the best adsorbent and the C–N one is the poorest for both substrates. There seems to be no direct relation between adsorptive power and catalytic effect since the Fe–C–N charcoal is the most active catalyst with the C–Fe one second and the unpromoted C–C charcoal poorest. What is especially striking is that the various charcoals show very much the same order of activity for all three catalytic processes. The one exception is the standing of the C–N and C–Fe charcoals as regards catalase action. The difference, however, is very small.

We cannot legitimately theorize with such limited data at hand, but we readily are led to think that there is some process common to all three catalytic actions. On thermodynamic grounds we should expect a catalyst good for the decomposition of hydrogen peroxide to be equally good for its formation. Does this indicate that oxidase action involves the formation of a peroxide as postulated by Lamb and Elder?[6] Then what is the function of charcoal in influencing reactions in the presence of peroxide? This question we attempt to answer in the second part of this paper.

2. The Effect of Charcoal Sols on the E. m. f. Produced by Hydrogen Peroxide Solutions. The Function of Charcoal in Oxidative Reactions.—In order to gain some idea of the role of charcoal in the so-called peroxidase reactions it is necessary to find some method which will enable us to estimate the relative oxidizing power of hydrogen peroxide in the presence and absence of charcoal. This immediately suggests the use of oxidation–reduction potentials. However, it has been pointed out that the oxidation–reduction potential of peroxide cannot be measured directly by the usual means.[7] Ort and his collaborators[8] have found that the voltages

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[3] King, *J. Chem. Soc.*, 889 (1935).

[4] The detailed analysis of the oxidase and peroxidase curves obtained with these charcoals will be made the subject of a separate investigation.

[5] Miller, *J. Phys. Chem.*, **30**, 1168 (1926), method (a).

[6] Lamb and Elder, THIS JOURNAL, **53**, 137 (1931).

[7] Bancroft and Murphy, *J. Phys. Chem.*, **39**, 337 (1935).

[8] Ort and Bollman, THIS JOURNAL, **49**, 805 (1927); Ort, *ibid.*, **50**, 420 (1928); *J. Phys. Chem.*, **33**, 825 (1929); Clifton and Ort, *ibid.*, **34**, 855 (1930); Roepke and Ort, *ibid.*, **35**, 3596 (1931); Ort and Roepke, *ibid.*, **38**, 1061 (1934).

developed in peroxide–sugar solutions are greatly affected by certain amino acids. The results of this investigation led these workers to the conclusion that an active, easily oxidized form of glucose exists in such solutions, but no conclusion was drawn as to the effect of the amino acid on the hydrogen peroxide.

In the first paper of this series[1a] we attempted a measurement of the voltages developed in hydrogen peroxide solutions in the presence of charcoal sols in order to determine whether the presence of colloidal charcoal had any influence upon the peroxidase reaction. Although the hypothesis involving the presence of colloidally dispersed charcoal has not been found necessary to explain our more recent results, the method seemed a suitable one for leading us to at least a partial answer to the question: what is the function of charcoal in oxidative processes?

By measuring the potentials developed across a bright platinum electrode and a saturated calomel electrode immersed in peroxide solutions with and without the addition of charcoal sols of various kinds, we can determine the specific effect of the charcoal upon the peroxide alone, as distinguished from any effect upon the reagents or products of any reaction we may choose to employ to test charcoal activity. The need for such work was felt especially in this Laboratory when we had to postulate the existence of an active form of oxygen in solution in order to explain the shape of the oxidase curves obtained in a previous study.[1b]

When we attempted to measure the potentials of peroxide solutions of different concentrations, we obtained widely varying results which were not duplicable. The voltages as read directly ranged from 0.56 to 0.45 v. for peroxide solutions varying between 0.5 and 0.05%. In the presence of charcoal sols, however, the voltage was easily measured and reproduced. This effect may be due to a speeding up of the attainment of equilibrium in a manner analogous to the effect of charcoal on the oxygen electrode.[6] Another effect is noted when the amount of charcoal sol added is varied and the concentration of the peroxide kept constant at 0.2%. The voltage progressively decreases as shown in Fig. 1, which also illustrates the irreproducibility of peroxide potentials in the absence of sufficient charcoal. Similar results were obtained with charcoal sols prepared in various ways from a wide variety of "pure" and commercial activated charcoals. In every case (some 150 experiments) the same type curve was obtained.

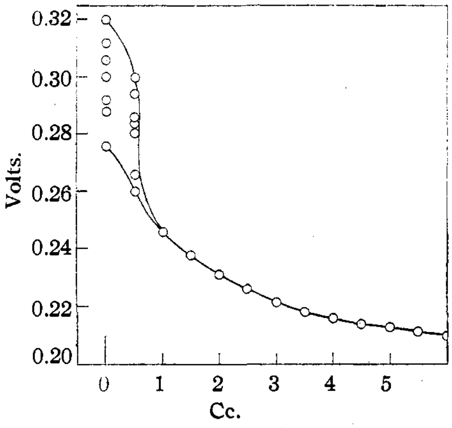

Fig. 1.—Voltage obtained from 0.2% hydrogen peroxide in the presence of varying amounts of charcoal hydrosol. With less than one cc. of sol the voltages were not duplicable.

In order to prove that it was the charcoal surface which produced this effect we studied the action of various charcoal poisons. Amyl alcohol prevented any dropping off of the voltage, and showed marked stabilizing power, giving an unvarying and reproducible voltage reading of 0.216 ± 0.0004 v. in the presence of varying amounts of charcoal. Potassium cyanide produced the same pair of results, but at a reduced voltage (0.027 v.). These findings indicate that it is an easily poisoned surface of charcoal which activates the hydrogen peroxide.

The explanation proposed for the shape of some of the oxidase curves obtained in this Laboratory[1b] is based upon experiments which indicate that charcoal will have the same effect upon oxygen. If air or oxygen is bubbled through distilled water a constant voltage is obtained between platinum and calomel electrodes after about fifty minutes (0.300 v. for oxygen, 0.260 v. for air). When the water is replaced by charcoal sol the voltages obtained are lower and become constant in a shorter time (0.250 v. for oxygen, 0.220 v. for air, in thirty-five minutes).

In view of these findings we believe that charcoal, independently of its possible effects upon the other reagents, has a definite effect upon hydrogen peroxide and oxygen, an effect which may be made to account in part for the oxidase and peroxidase properties of charcoal.

It may be objected that the peroxidase properties of charcoal are due solely to a combination of catalase and oxidase properties. This cannot be the case in the oxidation of uracil by hydrogen peroxide in the presence of charcoal[9] as shown in a previous paper.[1a] There we also stressed the fact that colloidal charcoal has definite peroxidase activity while lacking marked catalase activity. The latter property has now been investigated for a large number of charcoal sols. While 44 cc. of a 0.25 molar solution of hydrogen peroxide in a 100-cc. Pyrex flask liberated 3.0 cc. of oxygen in twenty minutes, when the water was replaced by a wide variety of charcoal sols, the yield of oxygen varied between 3.1 and 4.3 cc., a very small increase.

Experimental

Preparation of the Charcoals.—Approximately 190 g. of reagent-grade sucrose was suspended in 200 cc. of water in a porcelain vessel and heated until charring was complete. After grinding in an agate mortar, the product was activated for one hour in porcelain crucibles at 590 to 600°. Urea was added in the proportion of 5 parts to 95 of sucrose, while ferric chloride was added to the extent of 3%. The charcoals containing iron were washed repeatedly with distilled water until free from chloride before being activated.

Catalase Activity.—This was measured in a 100-cc. Pyrex flask, containing 100 mg. of the charcoal to be tested, 24 cc. of water, and 20 cc. of *p*H 7.5 citrate buffer. In a side-arm 1 cc. of superoxol was placed so that tilting the flask introduced it into the solution. The oxygen was measured in a 10-cc. gas buret while the flask was shaken 90 times per minute. In testing the charcoal hydrosols, the buffer and charcoal were omitted, and either 44 cc. of water or of charcoal hydrosol and 1 cc. of superoxol were used.

Preparation of the Charcoal Hydrosols.—Two general methods were used, the one described in the first paper of this series,[1a] and a new one involving the use of no diluent or foreign substance.[10] Some of the sols were stabilized with gelatin. In all cases the results were qualitatively the same as shown in Fig. 1, which represents the data for a gelatin protected sol obtained by the sodium chloride-grinding method. These sols contained in the neighborhood of 0.003 mg. of charcoal per cc.

Electrometric Measurements.—This work was performed as described originally[1a] except that only 4 cc. of 0.5% hydrogen peroxide was used. The results were duplicable within 3 mv. if one or more cc. of sol was present.

Summary

1. Several charcoals have been prepared and compared in catalase, peroxidase, oxidase and adsorptive properties.

2. The charcoals tested stand in the same order of activity for all three catalytic processes.

3. By electrometric means charcoal sols have been found to cause some activation of hydrogen peroxide and oxygen.

4. The catalase activity of the charcoal hydrosols prepared has been found to be very slight.

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[9] Schwob and Cerecedo, THIS JOURNAL, **56**, 2771 (1934).

[10] Schwob and Shea, unpublished research.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 69]

Studies in Organo-silicon Synthesis. I. The Wurtz Reaction with Silicon Chlorides

BY WALTER C. SCHUMB, JOSEPH ACKERMAN, JR., AND CHARLES M. SAFFER, JR.

Although numerous alkyl and aryl silanes have been prepared, and the field of organo-silicon chemistry has been explored extensively by Kipping and other investigators, it seemed worth while in the opinion of the writers to make a comparative study of compounds containing the linkages Si–C, Si–Si, and Si–X, leading to further knowledge of the stability of these bonds and of the reactivity of substituent groups as affected by the nature of the environment of the silicon atom.

The preparation of compounds of the type R_4Si and $R_3Si-SiR_3$, where R may be either alkyl or aryl, is generally effected by the Wurtz synthesis from SiX_4 and R_3SiX, where X is halogen. In some unpublished work[1] it had been determined that the Wurtz reaction, when applied to *p*-chlorobiphenyl and Si_2Cl_6, did not lead to the formation of hexaxenyldisilane but splitting of the Si–Si linkage occurred, and good yields of tetraxenylsilane were obtained. It was thought of interest, therefore, to determine whether this synthesis would be applicable to the preparation of other hexasubstituted disilanes, or whether cleavage of the Si–Si bond invariably would result.

The first synthesis tried was the preparation of hexaethyldisilane, $(C_2H_5)_3Si-Si(C_2H_5)_3$, which previously had been prepared by Friedel and Laden-

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[1] J. Ackerman, Jr., S. B. Thesis, M. I. T. 1936.