mixture was allowed to cool. All the potassium had disappeared and the reaction mixture was thick with precipitate. The mixture was filtered and the precipitate was dried. The precipitate was treated with water and extracted with ether. The ethereal extraction upon evaporation yielded 3 g. of crude di-*p*-tolyldisulfone melting at 214–218°. Recrystallization from benzene yielded crystals melting at 220–221°.

Summary

1. Diphenylcarbamine chloride and sodium or potassium yield tetraphenylurea and carbon monoxide with the intermediate formation of sodium or potassium diphenylamine.

2. Benzoyl chloride and sodium or potassium in anhydrous ether yield ethyl benzoate.

3. Acyl chlorides with sodium or potassium in xylene yield acid anhydrides.

4. *p*-Toluenesulfonyl chloride yields di-*p*-tolyldisulfone when treated with sodium or potassium in xylene.

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The Catalytic Properties of Charcoal. II. Further Studies on the Indophenol Reaction

BY JAMES F. O'BRIEN, VINCENT TKAC AND CLAUDE SCHWOB

The unusual factors encountered in a previous study of the activity of charcoal in catalyzing the hydrogen peroxide oxidation of a mixture of α-naphthol and *p*-phenylenediamine at *p*H 4.5 to form indophenol[1] prompted us to continue our studies of this interesting reaction.

Two aspects of this oxidation particularly suggest further investigation. What is the cause of the decrease in yield of the indophenol after one-half minute? What is the role of the charcoal in these oxidative reactions? In the present paper we attempt to give a partial answer to the first question. The third paper of this series will treat of certain findings relative to the second question.

We first repeated the original work[1] under carefully controlled conditions, using a so-called "pure" sucrose charcoal. At both 30 and 40° we confirmed our former findings, the yield being at a maximum at one-half minute and then decreasing to a value which remained constant after seven minutes. As before, the indophenol was found to be strongly adsorbed by the charcoal so that the latter and the filtrate were analyzed separately. Figure 1 shows the amount of indophenol present at various times. The charcoal furnished the bulk of the indophenol (curve 1), but a definite peak at one-half minute shows in the filtrate curve (curve 2).

The ratio of the total yields of the reaction at 40° to those of the reaction at 30° at corresponding times gives us a series of numbers which are

(1) Paper I. Schwob, THIS JOURNAL, **58**, 1115 (1936).

TABLE I

Time, min.	Temp. coeff.	E, cal.
0.25	1.083	1400
.5	1.138	2300
1	1.198	3300
2	1.238	3900
4	1.239	3900
7	1.239	3900
14	1.241	3900
28	1.245	4000

akin to temperature coefficients (Table I). It will be noticed that these ratios increase linearly with time until, after two minutes, they approach a constant value. A rough calculation of the apparent energies of activation for these reaction times was made by substituting these coefficients in the Arrhenius equation. It is to be emphasized that Hinshelwood[2] and others have pointed out that such a substitution cannot give the true energy of activation for a heterogeneous reaction. It is interesting to note, however, that the values obtained for E as well as for the temperature coefficients show that two distinct processes are going on in this reaction, one predominating in the first two minutes, the second one after that. The energy of activation was likewise determined for the uncatalyzed formation of indophenol at 30 and 40° (Fig. 1, curves 5 and 6), and found to be approximately 5000 cal.

The progressive increase in the value of E for the catalyzed reaction suggests either of two possibilities: the charcoal suffers poisoning as the

(2) Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," The Clarendon Press, Oxford, 1933, p. 348, *et seq*.
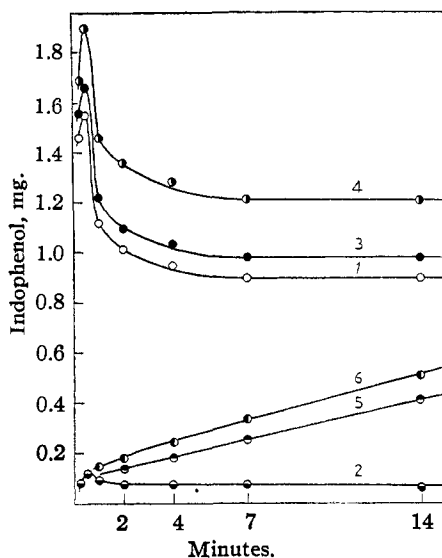
Fig. 1.—Curve 1, indophenol obtained from charcoal at 30°; curve 2, indophenol in the filtrate (30°); curve 3, total yield at 30°; curve 4, total yield at 40°; curve 5, yield at 30° in the absence of charcoal; curve 6, yield at 40°, no charcoal. The maximum yield in curve 4 is approximately 5% of the theoretical.

reaction progresses, or the indophenol is destroyed by a secondary reaction. Were the former true it seems likely that the amount of indophenol present would not decrease with time but, rather, would increase owing to the uncatalyzed reaction. The gradual destruction of indophenol remains as the only possibility consistent with the experimental facts, and we believe, on the strength of the following work, that this destruction not only takes place, but that the presence of charcoal is necessary. If this last is true, the addition of some charcoal-inhibiting agent when the reaction has proceeded one-half minute should prevent any subsequent falling off in yield.

The inhibitors tested were amyl alcohol and potassium cyanide, added when the reaction had progressed exactly one-half minute. As seen in Fig. 2, curve 2, the addition of amyl alcohol poisoned the charcoal to some extent, resulting in a constant yield much greater than that of the uninhibited reaction. The addition of potassium cyanide (Fig. 2, curve 3) completely stopped the destruction of indophenol and permitted a gradual increase in yield. This indicates that the removal of the charcoal from the field of action by means of cyanide not only prevents the destruction of indophenol but allows its formation to proceed at

the same rate as the uncatalyzed reaction (compare the latter portion of this curve with Fig. 1, curve 5).

What is the nature of this catalyzed destruction of indophenol? Recently, other investigators,[3] working on the catechol–tyrosinase reaction, obtained results similar to ours when insufficient enzyme was used to promote the oxidation of catechol, an effect which they attributed to secondary reactions between catechol and quinone. We felt it necessary to determine whether a similar condition would account for our results, that is, whether the reaction which destroys the indophenol involves excess reagents. Reducing the substrate concentration to one-quarter of the value used in former experiments, a curve was constructed for the reaction at 30° (Fig. 2, curve 4). The filtrate yields were negligible. Multiplying the constant value (1.38 mg.) obtained here by four to permit direct comparison with the other curves gives a constant yield value of 5.5 mg. This shows that in the presence of sufficient charcoal we have the apparent anomaly of lessened indophenol destruction. This can only be interpreted as proof that excess reagents are involved in the destruction of indophenol. Conversely, with substrate concentrations double those of the original experiments, final indophenol yields were obtained which were much lower than those formerly obtained.
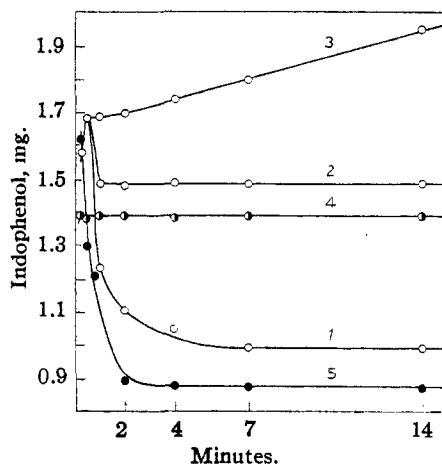

Fig. 2.—Curve 1, same as curve 3, Fig. 1; curve 2, effect of amyl alcohol; curve 3, effect of potassium cyanide; curve 4, one-quarter concentrations; curve 5, double concentrations.

Hence, we are led to believe that the indophenol destruction is catalyzed by charcoal and in-

(3) Dawson and Nelson, THIS JOURNAL, 60, 250 (1938).

volves a reaction with excess reagents (α-naphthol, p-phenylenediamine, and/or hydrogen peroxide). In fact, we found that indophenol adsorbed on charcoal is destroyed more rapidly when suspended in dilute hydrogen peroxide containing either α-naphthol or p-phenylenediamine than in the presence of peroxide solution only. Although, due to the difficulty of obtaining a sufficiently concentrated solution of pure indophenol in water, these experiments are at best qualitative, they are in good agreement with the above work.

What is the role of the peroxide? The catalytic effect of charcoal in promoting the oxidation by air or oxygen of many chemical individuals is well known. It was thought desirable to investigate the indophenol reaction in the absence of hydrogen peroxide, using air as the oxidant. This is analogous to the action of the enzymes known as oxidases as distinguished from peroxidases, and we consequently favor the use of the name "oxidase action" to denote this particular catalytic role of charcoal.
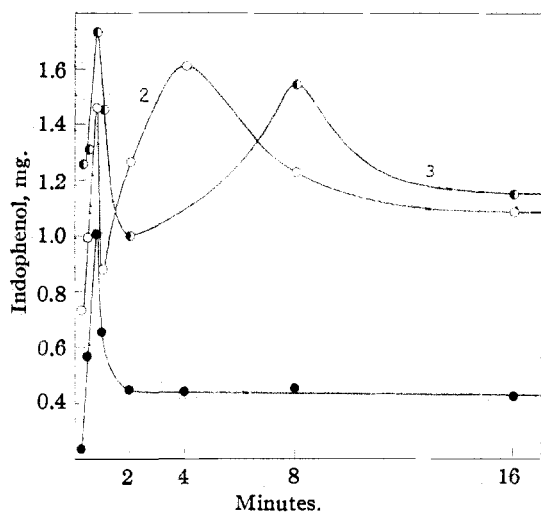

Fig. 3.—Curve 1, total indophenol yield at pH 4.5; curve 2, pH 6.5; curve 3, pH 7.5.

We first performed an experiment at pH 4.5 and 20°. The curve obtained (Fig. 3, curve 1) bears a striking resemblance to the peroxidase curves. Hence, we are inclined to think that the same factors predominate whether hydrogen peroxide or oxygen be the oxidant. Among these factors, the disappearance of indophenol is especially interesting. If peroxide is one of the substances involved in the disappearance of the dye, air must be an equally good reagent. How-

ever, if we consider the results of the quarter concentration peroxidase experiment (Fig. 2, curve 4), it becomes evident that neither peroxide nor oxygen is of as great importance in the destruction of indophenol as the other reagents. In that experiment, reducing the amount of α-naphthol and p-phenylenediamine without reducing the quantity of peroxide and having the reaction mixture fully exposed to air, resulted in comparatively little destruction of indophenol.

Variation in the hydrogen-ion concentration in the oxidase experiments led to results which are worth noting. The data concerning pH changes presented here apply only to oxidase action since it is probable that, due to the well-known catalase properties of charcoal, some oxidase action is likely to take place during the peroxidase reaction,[4] resulting in data difficult of interpretation. Moreover, the peroxidase reaction at pH's higher than 4.5 does not lend itself readily to kinetic study due to its rapidity.

A decrease in acidity to pH 6.5 in the oxidase reaction led, as was expected, to an increased yield of indophenol (Fig. 3, curve 2). More important, however, is the shape of the curve, two maxima now being evident, one at three-quarters of a minute, the other at four minutes. These results prompted us to increase further the pH to 7.5. Again an increased yield was noted, and again a second maximum appeared, but at eight minutes instead of four (Fig. 3, curve 3).

While performing these experiments, it was noted that ten or twelve seconds after the start of the reaction a deep red color (indophenol) appeared throughout the reaction mixture, only to disappear in three or four minutes. The presence of charcoal in suspension tends to obscure this color, but it is plainly visible by means of transmitted light.

These observations, while scarcely sufficient as a basis for theorizing, nevertheless have tempted us to formulate the following explanation as a working hypothesis to guide further experimentation.

We believe that each oxidase curve is of the same type, and is the resultant of two actions, reaching a maximum simultaneously or nearly so at pH 4.5, but successively at a higher pH. Let us consider the latter curves. The charcoal in some way activates the oxygen in solution,[5]

(4) That this combined catalase–oxidase action is not the sole catalytic effect in the peroxidase reaction has been pointed out previously,[1] and will be discussed more fully in Paper III of this series.

(5) This activation of oxygen by charcoal is suggested by experiments to be described in the next paper of this series.

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.

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-

(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).