[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE FRUIT PRODUCTS LABORATORY, UNIVERSITY OF CALIFORNIA]

The Kinetics of the Auto-oxidation of Catechol in the Presence of Several Foreign Substances

BY G. E. K. BRANCH AND M. A. JOSLYN

It is well recognized that many auto-oxidations are inhibited by small quantities of foreign substances.[1-5] As a rule this process destroys the inhibitor and its action is temporary. This phenomenon is readily explained only on the assumption of a chain mechanism for the auto-oxidation, and the existence of a typical temporary inhibition is one of the best indications for a chain mechanism for a thermal auto-oxidation.

Since we had studied the kinetics of the absorption of oxygen by moderately alkaline solutions of catechol[6] it seemed desirable to find out whether or not the reaction involved a chain mechanism. With this in view we measured the rate of auto-oxidation of catechol in the presence of a number of foreign substances. During these investigations we observed certain peculiarities in the behavior of catechol in the presence of small quantities of pyrogallol, hydroquinone, or resorcinol, which led us to investigate the auto-oxidation when a large proportion of catechol was replaced by one of these phenols.

Experimental

The experimental procedure was essentially that used for pure catechol.[6] The rates of absorption of oxygen were measured by changes in pressure at constant volume; the solutions were buffered by the mixture of KH_2PO_4 and K_2HPO_4 obtained on addition of catechol to 0.8 M K_2HPO_4; and the pH values of the solutions were obtained with a glass electrode. The solution was shaken sufficiently vigorously to maintain it saturated with oxygen. During each individual experiment the concentration of catechol and the pressure of oxygen were practically constant as the total amount of oxygen absorbed was small with respect to both the oxygen and the catechol in the reaction vessel. The only variation from our previous procedure was that the foreign substances were added to the catechol solutions, or to the phosphate buffer when some reaction in the catechol solution was expected. In our search for inhibitors the foreign substances were all 0.001 M and the catechol 0.1 M. In experiments with large quantities of foreign phenols, the total phenol concentration was maintained at 0.1 M but the proportion of catechol was varied.

The rates are expressed in cc. of oxygen at 25° and 1 atmosphere absorbed by 125 cc. of solution. The average error in the measurements is 7%, most of which is due to error in pH measurement. An effect of less than 10% is not considered as significant.

Data and Discussion

Effects of Small Quantities of Foreign Substances.—Under the conditions of our experiments, when pure catechol solutions are used, about 20 cc. of oxygen can be absorbed without the rate decreasing by more than 10%. This approximately constant rate is that of the first measurable step in the reaction between oxygen and catechol.

When the foreign substance is not oxidized specifically faster than catechol, the rate of absorption is also practically constant, and may be faster, slower or equal to that characteristic of pure catechol, according as the foreign substance acts as a catalyst, or an inhibitor or is without action on the absorption of oxygen by catechol.

When the foreign substance is oxidized specifically much faster than catechol, its concentration is reduced to practically zero before that of catechol has been affected greatly, for the foreign substances were always added in quantities very small with respect to catechol. The foreign substances were added in quantities equivalent to about 3 cc. of oxygen in a reaction in which one molecule of oxygen reacts with one of the foreign substance. The result is that the absorption rate changes at the beginning of the experiment but becomes approximately constant before the end. When the products of the oxidation of the foreign substance are without action on the absorption of oxygen by catechol, the approximately constant final rate is that of pure catechol, and may be recognized as such. In these cases the initial rate is slower or faster than the final rate according as the foreign substance is an inhibitor or accelerator of the auto-oxidation of catechol. A foreign substance that absorbs oxygen independ-

(1) Hans L. J. Bäckström, THIS JOURNAL, **49**, 1460 (1927).

(2) Hubert N. Alyea and Hans L. J. Bäckström, *ibid.*, **51**, 90 (1929).

(3) W. P. Jorissen and A. H. Belinfante, *Rec. trav. chim.*, **48**, 711 (1927).

(4) Charles Moureu and Charles Dufraisse, *Chem. Rev.*, **3**, 113 (1927); *J. Soc. Chem. Ind.*, **47**, 891 (1928).

(5) N. A. Milas, *J. Phys. Chem.*, **33**, 1204 (1929); THIS JOURNAL, **52**, 739 (1930); *Chem. Rev.*, **10**, 296 (1932).

(6) M. A. Joslyn and G. E. K. Branch, THIS JOURNAL, **57**, 1779 (1935).

ently of catechol, and at a specific rate ten times as fast as that of the auto-oxidation of catechol, would behave like an accelerator that is oxidized specifically much faster than catechol.

When the foreign substance is itself without action on the absorption of oxygen by catechol but is readily oxidized to a catalyst or inhibitor, the absorption starts at the rate characteristic of catechol but changes to that of a catalyzed or inhibited reaction. This final rate may be approximately constant if the product reaches a steady state concentration before the discontinuation of the experiment. This phenomenon is not restricted to substances that are rapidly auto-oxidized, for its oxidation may be induced by that of catechol. Resorcinol is an example of such a case. Catalytic or inhibitory actions of less than 10%, and independent absorptions of oxygen by the foreign substances less than ten times the specific rate of that by catechol are not observable in our experiments as they are indistinguishable from experimental fluctuations.

The data obtained are summarized in Table I,

TABLE I

OXYGEN ABSORPTION BY CATECHOL IN THE PRESENCE OF FOREIGN SUBSTANCE

Foreign substance	*p*H	Initial rate	Final rate	Rate in pure catechol
Ammonium chloride	8.3	3.4	3.4	3.3
Arsenious acid	8.3	2.8	2.8	3.3
Benzidine HCl	8.35	3.5	3.5	3.7
Cysteine HCl	8.3	0.1	3.2	3.3
Cystine	8.3	3.3	3.3	3.3
Gallic acid	8.3	3.8	3.8	3.3
Glycine	8.3	3.3	3.3	3.3
Hydroquinone	8.2	2.6	3.5	2.6
Indigo carmine	8.3	3.2	3.2	3.3
Maleic acid	8.3	3.1	3.1	3.3
Methylene blue	8.3	3.3	3.3	3.3
o-Aminophenol·HCl	8.3	0.8	3.2	3.3
p-Aminophenol·HCl	8.3	4.1	4.1	3.3
p-Hydroxybenzoic acid	8.3	3.3	3.3	3.3
Phenol	8.2	2.3	2.3	2.6
Picric acid	8.3	2.4	2.4	3.3
Potassium cyanide	8.3	3.3	3.3	3.3
Potassium iodide	8.2	2.4	2.4	2.6
Potassium sulfite	8.3	0.2	3.1	3.3
Potassium thiocyanate	8.3	3.2	3.2	3.3
Pyrogallol	8.2	4.8[a]	2.4	2.6
Resorcinol	8.2	2.7	3.6	2.6
Salicylic acid	8.3	3.2	3.2	3.3
Sodium phosphate	8.3	3.3	3.3	3.3
Tyrosine	8.3	3.2	3.2	3.3
Urea	8.3	3.3	3.3	3.3

[a] This is strictly a maximum rate, as in the first few seconds the rate is sensibly that for pure catechol.

which shows the initial and final rates, the *p*H values, and the rate in pure catechol at the same *p*H values. This table shows examples of all the cases discussed above, excepting that of an inhibitor that is formed during the reaction.

It is evident that most of the substances tested had practically no effect on the rate of oxygen absorption. Of the substances which maintained a steady rate, three, namely, arsenious acid, phenol and picric acid, exhibited a slight inhibition and two, gallic acid and *p*-aminophenol, showed slight catalytic action.

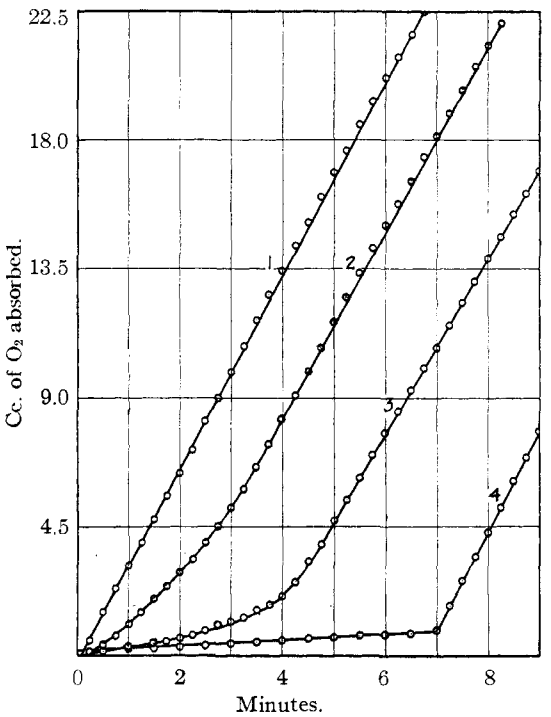

Fig. 1.—Rate of oxygen absorption by catechol at *p*H 8.3 in presence of: 1, no added substance; 2, *o*-aminophenol; 3, potassium sulfite and 4, cysteine hydrochloride.

It is evident from the data summarized in Table I and presented in more detail in Fig. 1 that *o*-aminophenol, cysteine and potassium sulfite are definite inhibitors for the reaction. The curves show reactions that are slow at first, but after a period rapidly change to the normal rates. This phenomenon is characteristic of an inhibited reaction in which the inhibitor is destroyed either in the act of inhibition or by the products of oxidation or both. This indicates that the absorption of oxygen by moderately alkaline solutions of catechol has a chain mechanism.

We have shown previously that the rate law for the oxidation of catechol in the range of *p*H value 6.5 to 10 is given by

$$V \propto (\text{cat}^-)(O_2)\ C/(C + A)$$

where C is the total concentration of catechol—being the sum of the concentration of dissociated and undissociated molecules—and A some constant. The kinetics can be accounted for on the assumption that "catechol," oxygen and the monovalent ion function in chain initiating and chain continuing processes and that "catechol" and solvent function in chain breaking processes.

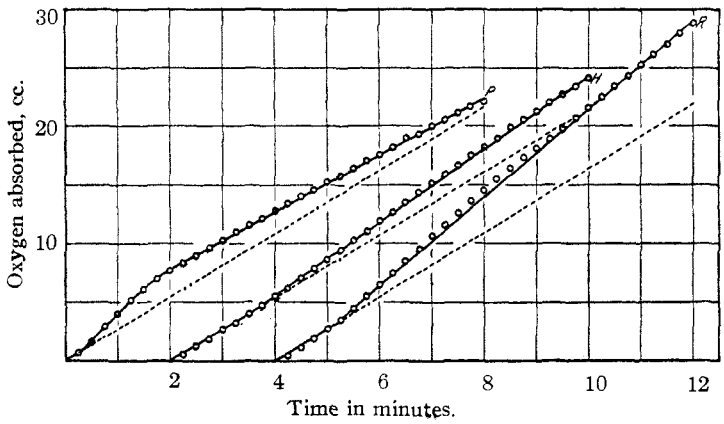

Fig. 2.—Rate of oxygen absorption by catechol in presence of small quantities of pyrogallol (P), hydroquinone (H) and resorcinol (R) at *p*H 8.3. The abscissas of the curves for H and R are displaced 2 and 4 minutes, respectively, to the right. The dotted lines show the rate in pure catechol.

The term "catechol" as used above refers to both the undissociated molecule and its ions. The constant A is the ratio of the specific rate of the chain breaking process of the solvent to that of catechol.

This mechanism also explains why so few of the chosen substances acted as inhibitors. For catechol is its own inhibitor, and the foreign molecule must compete in the chain breaking process with a hundred molecules of catechol.

The inhibition of cysteine is of special interest. Assuming that one molecule of oxygen can destroy four molecules of cysteine, about 0.75 cc. is sufficient to remove the cysteine added. After the absorption of 1 cc. of oxygen the cysteine is removed, as is shown by the appearance of the normal rate. This leads to the conclusion that cysteine is an extremely effective inhibitor and must almost completely *remove the chain character of the reaction*. This conclusion is further confirmed by the extremely sharp break in the cysteine curve between the inhibited and the normal absorption. The inhibited reaction is about 0.03 times the normal rate, and the length of the normal chain may be estimated as between 30 to 60 links.

Small amounts of pyrogallol, hydroquinone and resorcinol after an initial period in which they exerted practically no effect (which extends for about fifteen seconds for pyrogallol, one minute for resorcinol and one and three-fourths minutes for hydroquinone) appreciably increased the rate of oxidation of catechol (see Fig. 2). This increase in rate is maintained over more than five minutes by hydroquinone and resorcinol but the maximum rate reached in thirty seconds in pyrogallol is reduced in about two minutes to that of catechol alone.

Effect of Pyrogallol, Hydroquinone and Resorcinol in Large Quantities.—The rates of oxygen absorption by mixtures of catechol and pyrogallol, hydroquinone or resorcinol in which the mole fraction of the foreign phenol varied from 0 to 1.0 but at constant concentration of total phenol (0.1 M) are shown in Figs. 3 and 4.

It is seen from the data presented in Fig. 3, that pyrogallol and hydroquinone act as catalysts for the oxidation of catechol. But the type of catalysis is peculiar. Pyrogallol–catechol and hydroquinone–catechol mixtures oxidize at much faster rates than would be possible if the components of the mixture oxidized at rates independent of each other. In both mixtures a molal fraction of 0.2 of the more reactive phenol produces an oxygen absorption almost as fast as that of the more reactive phenol by itself. One way of explaining this phenomenon is to assume that either phenol can continue or break the chain initiated by either activated phenol. Then neglecting the chain breaking effect of the solvent

$$V = k_1 C \frac{a_{11}C + a_{12}P}{b_{11}C + b_{12}P} + k_2 P \frac{a_{12}C + a_{21}P}{b_{12}C + b_{22}P}$$

where V is rate; C and P the respective concentrations of catechol and pyrogallol or hydroquinone; a the rate constant for the chain continuing process, the subscript 11 referring to the chain initiated by C and continued by C, and 12 to the chain initiated by C and continued by P,

etc.; b the rate constant for the chain breaking process; and k_1 and k_2 the rate constants for the chain initiating processes for catechol and pyrogallol or hydroquinone, respectively. If the more reactive phenol is specifically much more efficient in both continuing and breaking the chains begun by either phenol, *i. e.*, $a_{12} > a_{11}$, $b_{12} > b_{11}$, $a_{22} > a_{21}$ and $b_{22} > b_{21}$, then

$$V = k_1 \frac{a_{12}}{b_{12}} C + k_2 \frac{a_{22}}{b_{22}} P \text{ (approx.)}$$

even when P is small with respect to C. If $k_1(a_{12}/b_{12})$ is approximately equal to $k_2(a_{22}/b_{22})$, the rate of oxidation of the mixtures of pyrogallol or hydroquinone and catechol is approximately that of the more reactive phenol of the same total concentration

$$V = k_2(a_{22}/b_{22})(P + C)\text{(approx.)}$$

The above explanation necessitates that the more reactive phenol be used up at a faster specific rate than catechol, so that when the concentration of the more reactive phenol is very small, its concentration would decrease appreciably while but little oxygen is absorbed. This would result in an observable decrease of the rate to that of pure catechol. This is true for molal fractions of 0.01 pyrogallol but is not true for hydroquinone at this concentration.

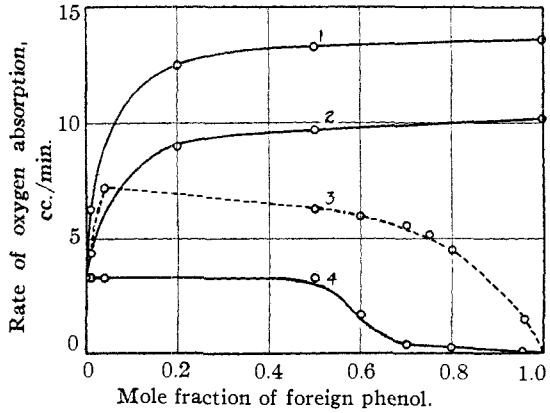

Fig. 3.—Rate of oxygen absorption at pH 8.3 by mixtures of catechol and the following phenols: 1, pyrogallol; 2, hydroquinone; 3, 4, resorcinol. Curve 3 is for first constant rates and curve 4 for initial rates. The pH values of the solutions were between 8.2 and 8.3. The rates are corrected to pH 8.3 on the assumption that the rates change with pH in the same way for the mixtures as for pure catechol. The error introduced cannot be significant.

Another possible explanation is as follows. Let us assume that chains of activated pyrogallol are longer than those of activated catechol; that any chain may be continued or broken by either phenol; that the length of the chain depends chiefly on the nature of the activated phenol and less on the nature of the phenol acted upon; and that a chain begun as an activated catechol chain may be converted into an activated pyrogallol chain, or *vice. versa*. If chains are initiated at approximately equal rates by catechol or pyrogallol, the rate of oxygen absorption in a mixture depends chiefly on the relative proportions of catechol and pyrogallol chains, but owing to the chain exchanging process this proportion is not that of the phenols in the mixture. Should the change of activated catechol to activated pyrogallol be specifically faster than the reverse process, then the pyrogallol chains would predominate and the rate approximate that of pure pyrogallol even when catechol is in excess.

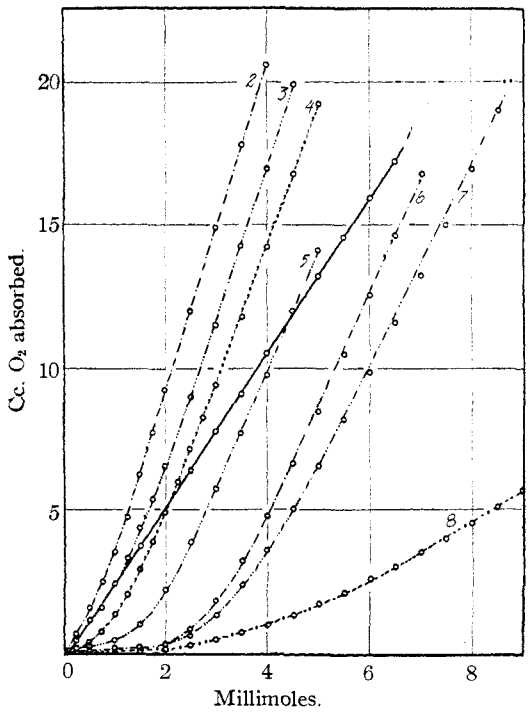

Fig. 4.—Rate of oxygen absorption at pH 8.2 by mixtures of catechol and resorcinol having the following mole fractions of resorcinol: 1, 0.0; 2, 0.04; 3, 0.5; 4, 0.6; 5, 0.7; 6, 0.75; 7, 0.8; 8, 0.96. The rate for pure resorcinol was measured as 0.0038 cc. of oxygen per minute at pH 8.3.

In this explanation of the phenomenon, the rate of oxidation of the more reactive phenol may, but need not, be specifically faster than that of catechol in mixtures of the two. It is therefore applicable to both pyrogallol and hydroquinone and is to be preferred.

When small quantities of pyrogallol or hydroquinone are used the initial rate is that of pure catechol and the catalysis does not show itself until a certain lapse of time (see Fig. 2). This would suggest that the chain exchanging process on which the catalysis depends occurs with an intermediate product of the oxidation of pyrogallol or hydroquinone, such as a deactivated peroxide. When larger quantities of pyrogallol or hydroquinone are used, the necessary intermediate is formed so quickly that the induction period is not noticeable.

The ideas presented may be clarified by the following mechanism for the delayed and limited catalysis of the oxidation of catechol by hydroquinone or pyrogallol provided the reader realizes that the formulation is schematic. In this formulation A refers to catechol, B to the more active phenol and activated molecules are starred. Initiation, continuation and termination of chains by B and termination of chains by the solvent have been omitted for the sake of brevity.

1. $A + O_2 + OH^- \longrightarrow AO_2^{-*}$ (chain initiating)
2. $AO_2^{-*} + A \longrightarrow AO_1 + A^{-*}$ (chain continuing)
3. $A^{-*} + O_2 \longrightarrow A^*O_2^-$
4. $AO_2^{-*} + A \longrightarrow AO_2 + A^-$ (chain breaking)
5. $AO_2^{-*} + B \longrightarrow BO_2 + A^{-*}$ (reaction upon which 6 must wait)
6. $BO_2 + A^{-*} \longrightarrow B^{-*} + AO_2$ (chain exchanging)
7. $B^{-*} + O_2 \longrightarrow BO_2^{-*}$
8. $BO_2^{-*} + A \longrightarrow B^{-*} + AO_2$ (continuing new chain)
9. $BO_2^{-*} + A \longrightarrow B^- + AO_2$ (breaking new chain)

Now if the specific rate of 6, k_6, is greater than that of 4, k_4, the chains in solution tend to become B chains as reaction progresses. Furthermore if $k_8/k_9 > k_2/k_4$ the new chains will be longer than the old.

In mixtures of catechol with small quantities of pyrogallol, the pyrogallol is used up specifically faster than is catechol and the rate soon becomes that for pure catechol; whereas, in mixtures of catechol and small quantities of hydroquinone, the maximum rate is maintained for a long time, showing that the composition of the mixture does not change much, the catechol and hydroquinone being oxidized at rates approximately proportional to their concentrations. Apparently, then, the essential difference between the behavior of pyrogallol–catechol and hydroquinone–catechol mixtures lies in the fact that pyrogallol is acted upon by the activated chains specifically faster than is hydroquinone. This is borne out by the longer induction period with hydroquinone.

The resorcinol–catechol mixtures, as seen in Fig. 3, differ from those of pyrogallol–catechol or hydroquinone-catechol in two important respects. In the first place, the induction periods, observable only when small concentrations of pyrogallol or hydroquinone are used, exist in all proportions of resorcinol to catechol and may last for a considerable duration of time. Secondly, the steady rates that are obtained eventually are higher than those obtained with either phenol alone. We have included, therefore, in Fig. 4 two curves for resorcinol, one for that of the steady rates and the other that for initial rates. But as the initial rates are often very slow the points on that curve are somewhat dubious.

The curves for the catechol–resorcinol mixtures are similar to those given by an inhibitor which is used up during the reaction, except that the final rate obtained is faster than that for catechol. It, therefore, is possible that we may be dealing with an auto-catalyst, resorcinol and small quantities of an inhibitor introduced with the resorcinol. The curve for the steady rates would not be affected by the introduced impurity but the curve of the initial rates would be that for reactions inhibited by an impurity. To test this we subjected the resorcinol to prolonged oxidation (about six hours) but the increase in the rate of absorption of oxygen which would be expected after the destruction of the inhibitor was not observed. The amount of oxygen absorbed in this test (over 1 cc.) was sufficient to have produced a marked increase in the rate of oxygen absorption by a catechol–resorcinol mixture. The experiment is not absolutely conclusive because it is possible that the oxidation of the inhibitor could be induced by that of catechol but not by that of resorcinol. However, we shall discuss the behavior of the catechol–resorcinol mixtures on the assumption that no inhibiting impurity was introduced with resorcinol.

The simplest explanation of the curve for the steady rates is that a rapidly oxidized intermediate is formed in the induced oxidation of resorcinol. This intermediate (probably a polyhydroxybenzene) acts like pyrogallol or hydroquinone in producing longer chains than those characteristic of either catechol or resorcinol. The curve is more complex than that for either pyrogallol–catechol or hydroquinone–catechol mixture because it is the result of the action of three components instead of two.

In the initial stages of the reaction we are dealing with the oxidation of mixtures of catechol and resorcinol before the resorcinol has been oxidized to the more active intermediate. The initial rates may be compared to those obtained in mixtures of pyrogallol or hydroquinone with catechol except that in catechol–resorcinol mixtures, catechol is the more instead of less active phenol. When mixtures of hydroquinone and catechol are oxidized there is a lag in the reaction during which the rate approximates that of the less reactive phenol followed by a steady rate approximating that of the more reactive phenol. This lag can be observed only when the time necessary for the formation of an intermediate in an amount sufficient to produce the steady rate is appreciable. This time varies inversely with the product of the concentration of the more reactive phenol by the true initial rate. Because of the fast initial rate in hydroquinone–catechol mixtures, this lag is observable only when small quantities of hydroquinone are present. The plot of observed initial rates against composition shows a double inflection as we pass from compositions in which the lag is observable to those in which it is not. The inflections for the hydroquinone–catechol mixtures occur very near to the axis representing 100% catechol. In the more inactive mixtures of catechol and resorcinol the inflections occur at about 50 mole per cent. of catechol.

The curve of the initial rates of oxygen absorption by catechol–resorcinol mixtures is therefore a combination of two phenomena. With high concentrations of catechol the measured initial rate is that characteristic of the mixture which has absorbed sufficient oxygen to give the maximum rate obtainable in absence of the formation of the more reactive intermediate from resorcinol. With smaller quantities of catechol the measured initial rate is approximately that of a mixture which has not absorbed sufficient oxygen to permit the change from the shorter resorcinol chains into the longer catechol chains.

Although it is thus apparent that the behavior of resorcinol–catechol mixtures can be explained in accordance with the general theory for pyrogallol or hydroquinone and catechol mixtures, the measurements seem to indicate an additional inhibitory action of resorcinol. This inhibition is shown in both the initial and steady-state rates obtained. The initial rates with small quantities of catechol are decidedly lower than those that would be expected for the same concentration of catechol in the absence of resorcinol, using the equation $V \propto [C^2/(C + A)]$. The steady-state rates obtained with large quantities of resorcinol are definitely lower than those with small quantities. This could be due either to inhibition by resorcinol or to the active intermediate being produced only in the induced oxidation of resorcinol. Inhibition by resorcinol would result if chains are shorter when they oxidize resorcinol than when they oxidize catechol, pyrogallol or hydroquinone.

At *p*H 8.3 the rate of absorption of oxygen by resorcinol (0.0038 cc./min.) is much slower than the rate of absorption by catechol inhibited by cysteine (0.1 cc./min.). If we accept the conclusion that in the cysteine inhibited reaction the chain is very short, the chain initiating reaction must be much slower for resorcinol than for catechol.

Acknowledgment.—We take this opportunity to thank Mr. Leo A. Joslyn for his aid in making the rate measurements.

Summary and Conclusions

1. The effect of a large number of foreign substances on the rate of oxygen absorption by catechol was studied. Most of these had little effect but cysteine, potassium sulfite and *o*-aminophenol behaved as genuine inhibitors destroyed during the reaction. Hydroquinone, resorcinol, pyrogallol, gallic acid and *p*-aminophenol appreciably increased the rate of oxygen absorption.

2. The oxidation of mixtures of catechol with pyrogallol or hydroquinone was studied at constant concentration of total phenol but varying proportions of the two phenols. The chief effect of pyrogallol or hydroquinone was to increase the rate of the reaction to almost that of pure pyrogallol or hydroquinone, respectively, over wide ranges of concentration of the latter. This is explained on a chain mechanism by the introduction of a chain exchanging process wherein a chain initiated by one phenol is convertible into a chain characteristic of the other.

3. In the presence of resorcinol, the initial rates are smaller than those of catechol alone, but these rates then increase until they are considerably greater than the rate for pure catechol.

This has been explained on the assumption that resorcinol is an inhibitor whose oxidation is induced by that of catechol to form poly-hydroxylbenzenes whose effects are similar to those of pyrogallol or hydroquinone.

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[CONTRIBUTION FROM SIR JOHN CASS TECHNICAL INSTITUTE]

The Reaction between Diphenylchloromethane and Ethyl Alcohol

BY F. G. KNY-JONES AND A. M. WARD

The results of a study of the rate of displacement of chlorine from diphenylchloromethane in ethyl alcoholic solution, obtained by Norris and Morton[1] differ in a number of respects from those obtained by one of us.[2]

Norris and Morton determined the velocity of the displacement from measurements of changes in the conductance of ethyl alcoholic solutions of the chloro compound, and concluded that the reaction is reversible, $CHPh_2Cl + EtOH$ (excess) $\rightleftharpoons CHPh_2OEt + HCl$, the direct reaction proceeding, under their experimental conditions, from 84.3 to 94.6% toward completion (Norris and Morton, Table IV, p. 1801); the factors which influenced this variation were not discussed, and the values of k for the postulated reverse reaction varied from 0.0015 to 0.0230. Ward[2] did not detect the reverse reaction in his kinetic study, which was based upon titration with alcoholic alkali of the hydrogen chloride formed. We did not obtain evidence of the reverse reaction by titrating alcoholic hydrogen chloride solutions of the final products.

Norris and Morton[1] (p. 1802) were unable to verify experimentally the calculated value for the reverse reaction and recorded but one experiment to show that the reaction was reversible; in this they passed hydrogen chloride into a solution of diphenylmethyl ethyl ether, dissolved in a mixture of dry benzene and petroleum ether, to which calcium chloride was added to remove the ethyl alcohol formed. The fact that they obtained diphenylchloromethane under these conditions does not afford any proof, however, of reversibility under the conditions of the kinetic experiments.

The velocity coefficients obtained by Ward (*e. g.*, k = 0.00341, 0.00349) are considerably higher than those of Norris and Morton (k = 0.00281 to 0.00310), which are higher also than those of Norris and Banta (k = 0.00266).[3] The values of k for the forward reaction were found to increase rapidly with increase in the water content of the alcohol, and the differences in the three sets of results may well be due to varying small amounts of water in the alcohol. According to Norris and Morton[1] (Table V, p. 1801) the extent of the reverse reaction diminished with increasing concentrations of water present. The equilibrium constant (K) for the reactions

$$CHPh_2Cl + EtOH \text{ (excess)} \rightleftharpoons CHPh_2OEt + HCl$$

is given by

$$K = \frac{k_1}{k_2} = \frac{[CHPh_2OEt][HCl]}{[CHPh_2Cl]}$$

where k_1 is the velocity coefficient of the forward reaction, k_2 that of the reverse reaction, and equilibrium concentrations are shown in square brackets. If the initial and equilibrium concentrations in g./mole/liter of diphenylchloromethane are C and $(1 - \alpha)C$, under the conditions of Norris and Morton's experiments $k_1/k_2 = \alpha^2C/(1-\alpha)$. The percentage conversions, calculated from their data (Table V), are shown.

Water, % by weight	0.15	0.58	1.07
Formality of $CHPh_2Cl$	.0990	.1191	0.1065
$k_1 \times 10^5$	316	358	407
$k_2 \times 10^4$	26	12	9
Conversion, %	93.0	96.3	97.8

Even if some 0.5% of water were present, about 4% of chloro compound should therefore be unchanged.

The failure to detect the reverse reaction in Ward's experiment might be due (1) to continued hydrolysis during the titrations, which were carried out by addition of alcoholic sodium hydroxide to a sample of the reaction mixture. Norris and Morton[1] (p. 1802), in checking results obtained by their conductivity method, added the reaction mixture to ice-cold water, removed cloudiness by means of carbon bisulfide, and then

(1) Norris and Morton, THIS JOURNAL, **50**, 1795 (1928).
(2) Ward, *J. Chem. Soc.*, 2285 (1927).
(3) Norris and Banta, THIS JOURNAL, **50**, 1804 (1928).