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Factors Influencing the Oxidation of Phenols, Catalyzed by Zinc Oxide and Light

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The rates of formation of peroxides under varying conditions of concentration of various phenols, temperature and light intensity, have been measured in aerated aqueous suspensions of zinc oxide in ultraviolet light at 3650 Å. At concentrations of 10^{-3} *M*, 20°, the relative rates of accumulation of peroxide decrease with added phenol in the following order: resorcinol, phenol, hydroquinone, catechol and pyrogallol. The latter two show considerable darkening in the early stages of the reaction particularly at higher temperatures. At equal concentrations of phenol, temperature and light intensity the maximum concentration of peroxide is the same for all five phenols. For each phenol there is a particular concentration for optimum initial rate. The stoichiometry indicates that the maximum concentration of peroxide in moles per liter is 4–5 times that of the original phenol. There is also an optimum temperature in the neighborhood of 20°.

Introduction

Previous work[1] on the formation of peroxides in aqueous suspensions of zinc oxide containing organic substances, when irradiated by light which only the zinc oxide absorbs, indicated a high degree of destructive oxidation of the organic material. In fact this system appears to offer good possibilities for studying relative rates of oxidation of various organic compounds at room temperature, since the active oxidizing agents formed on the surface are apparently powerful and non-specific. Recently an independent study of the same system has appeared in publication,[2] and the results concur with ours in most of the main points; particularly noteworthy is the fact that the maximum quantum yield for hydrogen peroxide was also found to be 0.5 in weak light intensity. Since sodium formate was used as the additive rather than phenol the results are not quantitatively comparable beyond this point.

However, we have found that resorcinol forms peroxides even faster than phenol, so that the quantum yield can even exceed 0.5. The evidence of Rubin, *et al.*,[2] as well as ours and Wagner's[3] favors the interpretation that electron transfer occurs between excited zinc oxide and substrate.[4] By the statement[2] that the theoretical maximum quantum yield is 0.5 we presume it is meant that two electrons are needed to reduce O_2 to peroxide. On the other hand if $\cdot O_2^-$ is formed first, it would be a radical ion, and hydrogen abstraction from an organic molecule may follow to produce a hydroperoxide ion HO_2^-; this would give a possible quantum yield of more than 0.5. Since previous work[1] has shown that peroxide is formed in absence of organic material, it is also possible that: $\cdot O_2^- + H_2O \rightarrow HO_2^- + \cdot OH$; in this case hydrogen abstraction and chain oxidation of the organic material would proceed by way of the hydroxyl radicals.

The purpose of the present work was to investigate more thoroughly the factors that favor accumulation of peroxide, and to follow the course of the reaction to completion in order to determine the maximum concentration of peroxide attainable, and the rate of decomposition. Phenol, with one hydroxyl group, resorcinol, hydroquinone and catechol, with two, and pyrogallol with three, were selected for study. We expected to get the largest amount of peroxide from phenol, since it is initially in the lowest oxidation state, and the least from pyrogallol, with the three dihydroxy compounds somewhere in between. Instead we found that the maximum amount of peroxide formed was approximately the same in all five solutions at 20° and concentrations of 10^{-3} *M*, but the rate of attaining this maximum was very different. Resorcinol formed peroxides most rapidly, and pyrogallol which is ordinarily considered very easily oxidized was extremely slow (Fig. 1). The effects of concentration and temperature were studied in some detail.

Experimental

The apparatus and method of procedure were the same as described.[1] Samples of one ml. were withdrawn at short intervals and analyzed for peroxide. The peroxide was assumed to be largely hydrogen peroxide; if some part was organic peroxide it was probably immediately hydrolyzed under the analytical conditions (in dilute sulfuric acid). Iodide and titanium sulfate procedures gave identical results in all cases. We have worked with samples of cumene, thymol and menthone hydroperoxides,[5] and have found that the first reacts only very slowly with $Ti(SO_4)_2$, the others react within a few minutes; all react rapidly with iodide ion. Our unknown peroxides react instantaneously with $Ti(SO_4)_2$ but only slowly with iodide ion unless catalyzed by molybdate. Furthermore the peroxide can be destroyed by catalase.

The Hanovia high pressure quartz mercury arc lamp was used throughout with a Pyrex jacket to retain all radiation below 3200 Å. which might affect the phenol directly. Oxygen was supplied by rapid entrainment of air. In each case 0.1 g. of zinc oxide and 25 ml. of phenol solution were used. Initial rate studies and long-period studies were carried out on separate samples so that the total volume of solution irradiated was never changed by more than 20% during the course of a run. The effect of light intensity in the present experiments was studied qualitatively by changing the distance from the lamp to the reaction vessel.

Results

Figure 1 shows the course of the formation and disappearance of peroxide at 20° from the five phenols. The maximum amount, 8–9 meq./ml., can be shown to depend on the particular conditions of the temperature and concentration rather than

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[1] M. C. Markham and K. J. Laidler, *J. Phys. Chem.*, **57**, 363 (1953).

[2] T. R. Rubin, J. G. Calvert, G. T. Rankin and W. MacNevin, THIS JOURNAL, **75**, 2850 (1953).

[3] C. Wagner, *J. Chem. Phys.*, **18**, 69 (1950).

[4] Previously we suggested that the electron might be transferred to water. This conclusion was based on the fact that water-soluble monomers would polymerize readily in this system in absence of O_2, whereas they could not be made to do so in anhydrous benzene. However, we are now engaged in studying oxidation of anhydrous alcohols to peroxides, for example on zinc oxide in absolute methyl alcohol. In this case, at least, the transfer must be directly to oxygen.

[5] Supplied to us through the courtesy of Dr. Paul Holmes of Monsanto Chemical Corp.

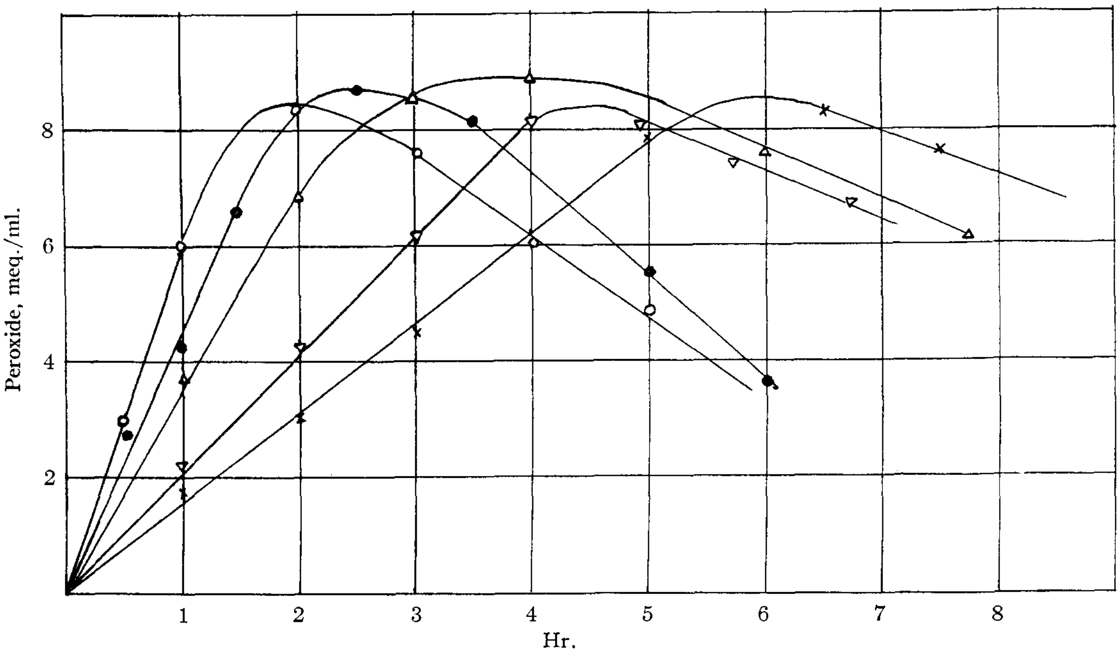

Fig. 1.—Rate of photoöxidation of phenolic compounds, 10^{-3} *M*, in aqueous suspensions of zinc oxide at 3650 Å., 20°; ○, resorcinol; ●, phenol; △, hydroquinone; ▽, catechol; ×, pyrogallol.

the nature of the organic substance. After this amount has accumulated, the peroxide begins to disappear at comparable rates in all five solutions at a given temperature. The fact that this rate is a little slower than that of hydrogen peroxide alone under similar conditions (Fig. 2) suggests that there are still small amounts of organic material contributing to its formation. This is further borne out by Fig. 3, which shows the decrease in concentration of the phenolic compound (absorption ~2700 Å.) in a 10^{-3} *M* solution of resorcinol that has been irradiated 2 hr., and should therefore be at the maximum point on the graph of Fig. 1.

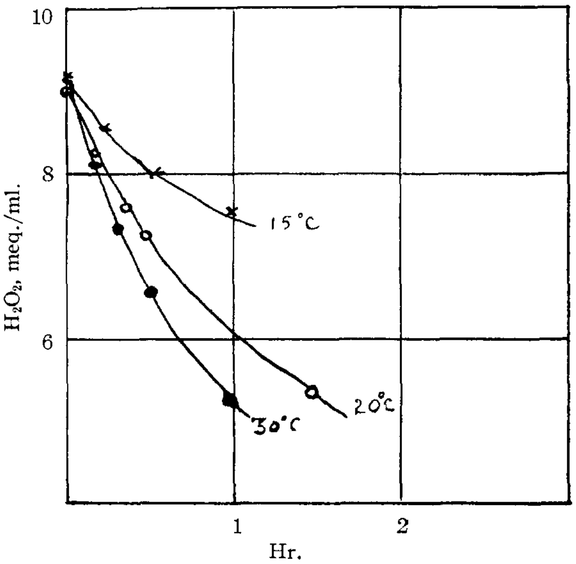

Fig. 2.—Rate of photo-decomposition of hydrogen peroxide in aqueous suspensions of zinc oxide at 3650 Å. at various temperatures: ×, 15°; ○, 20°; ●, 30°.

At 10° a similar set of curves is obtained, but the maximum reached is a little lower, 6–7 meq./ml.; the initial rates are slower except for catechol and pyrogallol, which appear to have no measurable activation energies, and the rate of disappearance of peroxide is also slower. At 30° the initial rates are almost the same as at 20°, perhaps a little higher in the first couple of minutes, but the rate of falling off is much greater, and the maximum reached is

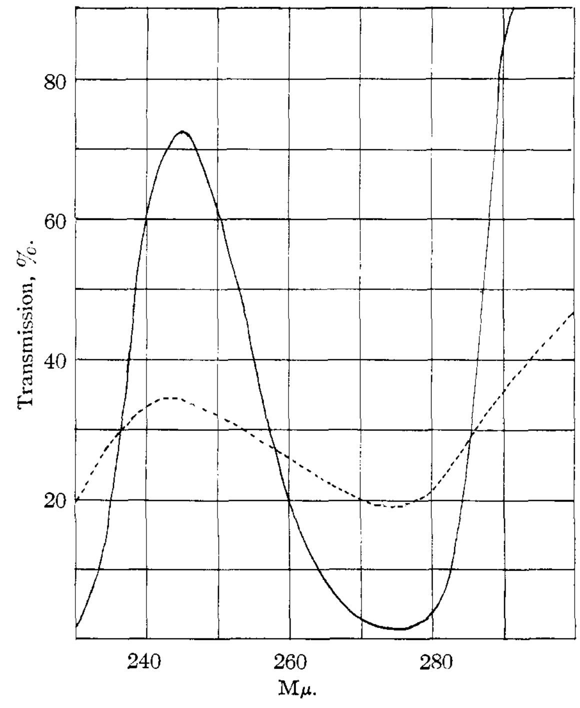

Fig. 3.—Absorption spectra of 10^{-3} *M* solutions of resorcinol (—) before and (---) after irradiation in the presence of zinc oxide for 2 hours, 20° (Beckman spectrophotometer).

again less than at 20°, 7–8 meq./ml. A comparison of the curves for 10^{-3} *M* phenol at these three temperatures is shown in Fig. 4. Similar relationships hold for all the other phenols. Therefore, there is an optimum temperature somewhere in the neighborhood of 20°.

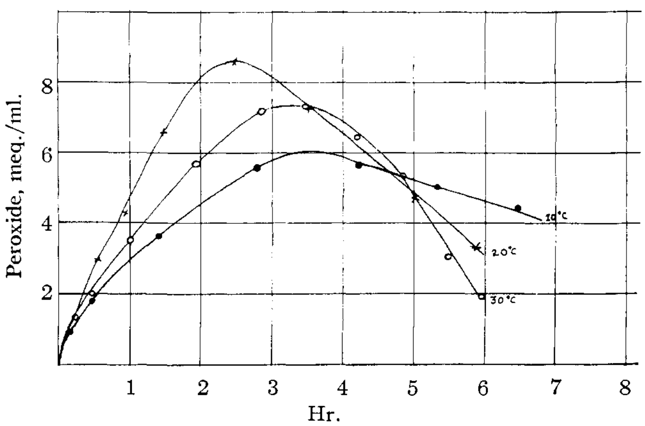

Fig. 4.—Rate of photoöxidation of phenol (10^{-3} *M*) in aqueous suspensions of zinc oxide at 3650 Å. at various temperatures: ×, 20°; ○, 30°; ●, 10°.

Since the decomposition of hydrogen peroxide has a greater activation energy than the formation of peroxide from the organic material, it is not surprising that the maximum amount formed is less at 30° than at 20°; however, the fact that the maximum is less at 10° than at 20° seems to indicate that some final step fails to occur at the lower temperature.

On comparing with Fig. 4[1] it is seen that the appearance and disappearance of polyhydroxy compounds in the photoöxidation of phenol was followed and found to describe the same type of curve as that of peroxide. It is also noted that after several hours of irradiation it is impossible to obtain any further test for phenols. Therefore the steady state concentration indicated in Fig. 5 is about the same as that obtained in the absence of organic material. This may be due to the reaction of $\cdot O_2^-$ with water as suggested above.

The results of the investigation on the effect of concentration show large differences depending on the nature of the phenol. Each has its own optimum concentration. Figures 5 and 6 show the results for catechol and resorcinol. Phenol resembles resorcinol most closely; the optimum concentration for both is about 10^{-3} *M*. Pyrogallol behaved like catechol. Both go most rapidly to peroxides around 10^{-4} *M*. For hydroquinone the optimum concentration is around 5×10^{-4} *M*.

There are a few additional factors which must be considered in an attempt to interpret these results. All these suspensions produce peroxide more rapidly at higher light intensity, but the increase is proportional to a little less than the square root of the light intensity. Therefore, while the over-all reaction is faster at high light intensity, the quantum yield is greater in lower light intensities in agreement with ref. (2) and F. D. Richardson.[6] Where the rate of formation of peroxide is decreased at higher temperatures or concentrations of phenol, there is a great deal of dark-colored polymer formation, probably of humic acid type. This is especially noticeable for catechol and pyrogallol, and evidently competes with peroxide formation. Under some conditions dark amorphous powders precipitate. Solutions of these dark polymers in either acid or basic solutions show general absorption throughout the ultraviolet and blue regions of the spectrum. They appear to be polyphenolic compounds since they can be extracted from acidified but not alkaline solutions with ether.

For a given concentration of catechol, for example, there are less of these dark colored intermediates at higher light intensity, and more peroxide. As the light intensity is increased the amount of catechol needed to produce a given amount of inhibition increases also. The exact mechanism of the inhibition remains to be discovered. The kinetics indicate that the primary oxidation product, either a free radical or a quinone, reacts with molecules of the original substances to produce polymers, possibly according to the mechanism proposed by Mason[7] for the enzymatic formation of catechol melanin. However, the dark polymer is not the final product in the zinc oxide suspension. Eventually it is completely oxidized to colorless products.

A similar inhibition due to excess hydrocarbon has been observed in the nitrogen dioxide sensitized photosynthesis of hydroperoxides by oxidation of hydrocarbons during smog periods.[8] In this case it has been suggested that the effect is due to quenching, an explanation which does not seem

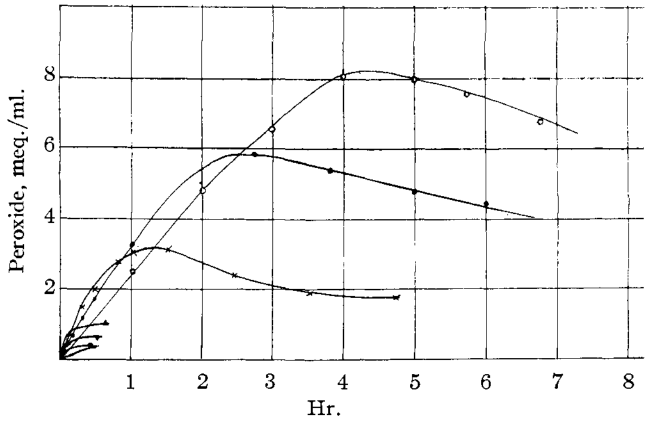

Fig. 5.—Rate of photoöxidation of catechol at various concentrations in aqueous suspensions of zinc oxide at 3650 Å., 20°: ○, 10^{-3} *M*; ●, 7.5×10^{-4} *M*; ×, 5×10^{-4} *M*; △, 10^{-4} *M*; ▽, 5×10^{-5} *M*; □ 10^{-5} *M*; —, no catechol added.

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[6] F. D. Richardson, private communication. *Cf.* E. Rabinowitch, "Photosynthesis, I," Interscience Publishers, Inc., New York, N. Y., 1945, p. 73.

[7] H. S. Mason, *J. Biol. Chem.*, **180**, 235 (1949), or article by H. S. Mason in "Pigment Cell Growth," ed. by M. Gordon, Academic Press, Inc., New York, N. Y., 1953, p. 277.

[8] A. J. Haagen-Smit, C. E. Bradley and M. M. Fox, Report to the Los Angeles County Air Pollution Control District (March, 1952). See also *Ind. Eng. Chem.*, **44**, 1342 (1952).

applicable to zinc oxide as a photosensitizer.

If $\cdot O_2^-$ is formed by the light on the surface of the zinc oxide, and the crystal is then left deficient in electrons, both the $\cdot O_2^-$ and an oxygen atom at the point of electron deficiency would be capable of removing either a hydrogen atom or an electron from a phenol molecule, and the net result would be the rapid initiation of chains similar to those supposed to involve free radicals in autoöxidations.

We have suggested[1] that the inhibitory effect of excess phenol might be due to covering the surface to the exclusion of water or oxygen. However, detailed studies of the adsorption of these phenols on zinc oxide in the dark fail to show any positive correlation. Phenol is only very slightly adsorbed in dilute solution, but the initial oxidation reaction is rapid. It is still adsorbed to only a small extent (about $^1/_{10}$ of the surface) at the concentration where it begins to show inhibition.

Amount adsorbed on 0.1 g. of ZnO (moles × 10^6) in 25 ml.

Concn., moles/l.	Resorcinol	Catechol	Hydroquinone	Phenol	Pyrogallol
1×10^{-4}		0.5	0.75	0.2	1.75
2.5×10^{-4}	1	0.5	1.75	.25	
5×10^{-4}	2.5	2.0	2.25	.50	3.5
1×10^{-3}	2.5	6.0	4.5	.8	4.5
2×10^{-3}		6.5		1.0	
5×10^{-3}			4.0		4.5
1×10^{-2}		6.2	4.5		

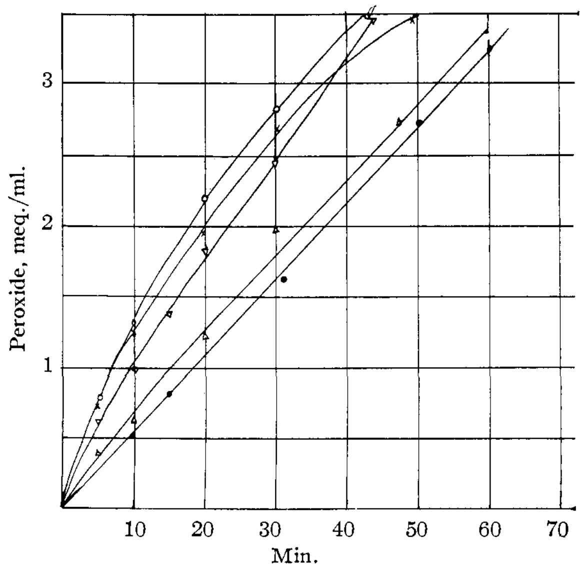

Fig. 6.—Rate of photoöxidation of resorcinol at various concentrations in aqueous suspensions of zinc oxide at 3650 Å., 20°: ○, 10^{-3} *M;* ×, 5×10^{-4} *M;* ▽, 5×10^{-3} *M;* △, 10^{-2} *M;* ●, 10^{-1} *M.*

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Pyrolysis of Mixtures of Acetone and Acetone-d_6

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Mixtures of acetone and acetone-d_6 were pyrolyzed at a variety of temperatures from 466–525° and the products examined. It is found that a Rice–Herzfeld mechanism is consistent with the facts, with the exception of the chain terminating reaction. Methyl ethyl ketone is not observed in the products but diacetone and ethane are present in small amounts. The activation energy difference for the abstraction of deuterium and hydrogen from acetone by methyl-d_3 radicals is 1.67 ± 0.09 kcal./mole. A brief investigation has been made of the effects of added carbon monoxide, propylene and iodine.

Recently[2] it was shown that the thermal decomposition of acetone at 500° proceeds almost entirely by a free radical mechanism. The Rice and Herzfeld mechanism[3] has been written as

$$CH_3COCH_3 \longrightarrow CH_3 + CH_3CO$$
$$CH_3CO \longrightarrow CH_3 + CO$$
$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3$$
$$CH_2COCH_3 \longrightarrow CH_3 + CH_2CO$$
$$CH_3 + CH_2COCH_3 \longrightarrow CH_3CH_2COCH_3$$

There is good evidence in the literature for the first four reactions[4] but no evidence for the last. The only evidence reported for the existence of methyl ethyl ketone in the products of acetone decomposition is that of Allen[5] for the photolysis.

A quantitative study has been made of the relative rates of formation of the various methanes from the pyrolysis of mixtures of ordinary and deuterated acetones as functions of temperature from 466–525°. There is no methyl ethyl ketone in the products, but ethane and diacetone are present and are possible chain ending products.

Experimental

1. **Preparation of Materials. A. Acetone.**—Commercial acetone which had been distilled through a Widmer column was further purified by the sodium iodide method of Shipsey and Werner,[6] and again distilled through a Widmer column. The resulting material was then distilled *in vacuo* through a column of drierite and a column of P_2O_5 in tandem. Mass spectrometer analysis showed no impurity above mass 58 and no water. This acetone was used for the kinetic experiments and for the preparation of deuteroacetone.

B. Acetone-d_6.—A modification of the method of Halford, Anderson, Bates and Swisher[7] was used for the deu-

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[1] Professor of Chemistry, New York University. Work performed at NOTS while on leave from regular duties.

[2] J. R. McNesby, T. W. Davis and A. S. Gordon, *J. Chem. Phys.*, **21**, 956 (1953).

[3] F. O. Rice and K. F. Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[4] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 132–138.

[5] A. O. Allen, THIS JOURNAL, **63**, 708 (1941).

[6] J. K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[7] J. O. Halford, L. C. Anderson, J. R. Bates and R. D. Swisher, THIS JOURNAL, **57**, 1633 (1935).