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PERACETIC ACID OXIDATION OF

LIGNIN MODEL COMPOUNDS

Ron McKelvey

Senior Thesis, Paper Technology

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Peracetic acid is being used to a limited extent as a
bleaching agent for newsprint (1) , and to a lesser extent,
as a pulping agent, at least at the laboratory level (2).
Haas, Schoch, and Ströle (3) report that peracetic acid is
an excellent reagent for the preparation of holocellulose
from wood. Ogait (4) also found that bleached cellulose
could be obtained in 60 to 65% yield from wood and straw
by the reaction of peracetic acid at 60 to 80° C. Haney,
Martin, and Sherk (5), and Poljac (6) have patented methods
of oxidizing lignin in wood by peracetic acid. The high
yields often obtained in bleaching, and excellent physical
properties that it gives the sheet, make peracetic acid a
very promising method, but high cost and instability have
limited the extent of its use. Also, Baily and Dence (7)
found peracetic acid inferior to chlorine dioxide for bleaching,
in contrast to an earlier, more optimistic report by Wayman,
Anderson, and Rapson (8).

THE NATURE OF PERACETIC ACID

Peracetic acid belongs to the class of compounds known
as peroxy acids. Peroxy acids are the most powerful oxidizing
agents of all organic peroxides. However, they are also
the least stable, hydrolyzing slowly in water to form hydrogen
peroxide and the corresponding carboxylic acid. Hackel, Kut-
kiewicz, and Kuboszek (9) have studied the explosive properties
of peracetic acid solutions at various concentrations. It is

reported that the explosion point for very concentrated solutions is about 110° C. Peracetic acid does not, however, explode upon impact, as do some peroxides.

An excellent review of peroxy acids is given by Swern (10), where he gives the following physical properties for peracetic acid:

Melting Point: 0.1° C
Boiling Points: 20-30° at 10-20 mm
                   25° at 12 mm
                   35-36° at 29 mm
                   105° at 760 mm
Explosion Point: 110° C

Peracetic acid reacts strongly with cork, rubber, and skin, and therefore must be handled carefully in the laboratory. Its decomposition is catalized by metal ions, and thus, its aqueous solutions can be stabilized by the addition of EDTA (11).

SOME REACTIONS OF PERACETIC ACID WITH AROMATIC COMPOUNDS

A survey of the literature indicates that a wide variety of reactions is possible, depending upon experimental conditions (see Table I). Böeseken and co-workers (12-20), who did most of the early work in this area, reported reactions usually producing cis, cis-muconic acid and related compounds. In several cases, however, they noted the formation of quinones, carbon dioxide, and in at least one instance (21), the formation of "a black, infusible powder, insoluble in KOH", presumably carbon. Wacek (22), Grundmann and Trischmann (23),

and Wacek and Fiedler (24) also reported the formation of open ring, muconic acid derivatives in the oxidation of phenols. Davidge et al. (25), however, indicated the formation of 1,4-benzoquinones in the oxidation of phenolic ethers. Most of these reactions were carried out in glacial acetic acid as solvent.

The reactions of peracetic acid are said to be very similar to those of chlorine dioxide and sodium chlorite (26), which have been studied in greater detail. Sarkanen, Kakehi, Murphy, and White (27) studied the oxidation of vanillin using chlorine dioxide, and gave an extensive treatment of the proof of structures, including some cleaved ring structures. Dence, Gupta, and Sarkanen (28) investigated the reactions of other lignin model compounds with chlorine dioxide and sodium chlorite. In some cases (27) only a fraction of the rings were cleaved, while in other instances (26), almost all aromatic nuclei appeared converted to the corresponding muconic acid derivatives.

Friess, Soloway, Morse, and Ingersoll (29) studied the reactions of perbenzoic acid with six different methoxy benzenes, and found some ring opening and some oxidation to quinone structures. They also stressed that the nature of the solvent is of fundamental importance in these oxidations. There appeared to be different reactivities in benzene and chloroform.
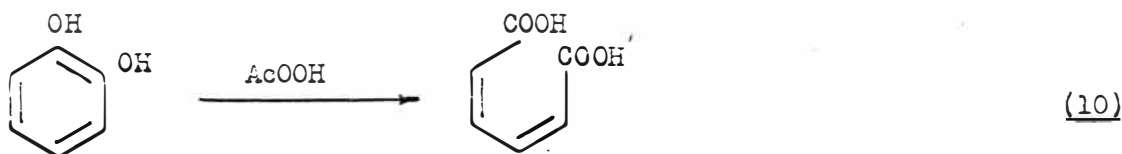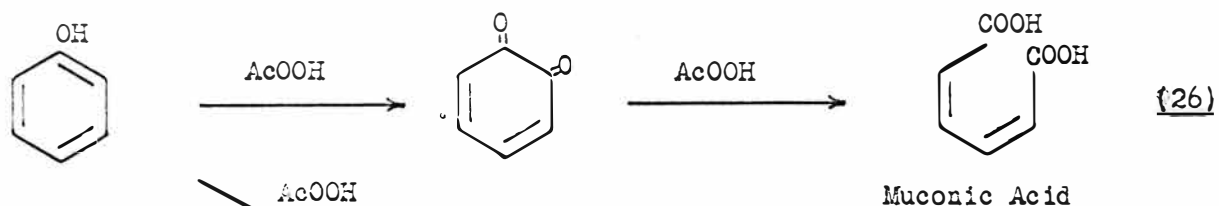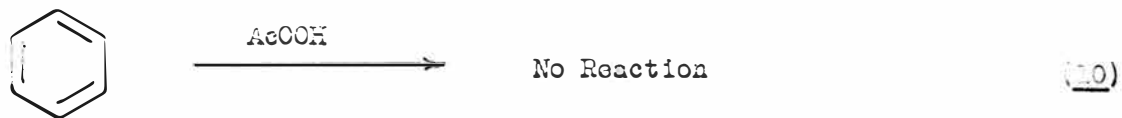
Rapson (30) found that the bleaching reactions of per-acetic acid are extremely dependent upon pH, a fact that has

Table I

Reactions from the Literature
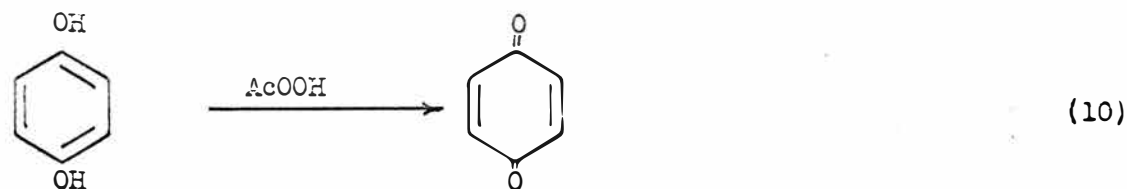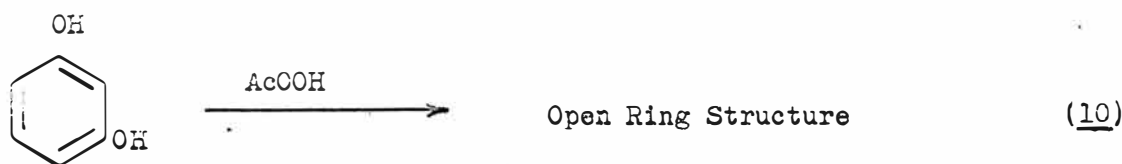
Peracetic Acid and Aromatic Compounds

Ref.

Benzene $\xrightarrow{\text{AcOOH}}$ No Reaction ... (10)

Phenol $\xrightarrow{\text{AcOOH}}$ (dienone) $\xrightarrow{\text{AcOOH}}$ Muconic Acid (COOH, COOH) ... (26)

Phenol $\xrightarrow{\text{AcOOH}}$ (quinone) ... (26)

Catechol $\xrightarrow{\text{AcOOH}}$ (COOH, COOH) ... (10)

Resorcinol (OH, OH) $\xrightarrow{\text{AcOOH}}$ Open Ring Structure ... (10)

Hydroquinone (OH / OH) $\xrightarrow{\text{AcOOH}}$ (quinone, O / O) ... (10)

Table I (cont'd)

Ref.

Reactions of Peroxy Acids with Aromatic Compounds

(25)

(29)

(29)

(29)

(29)

Table I (cont'd)   Ref.
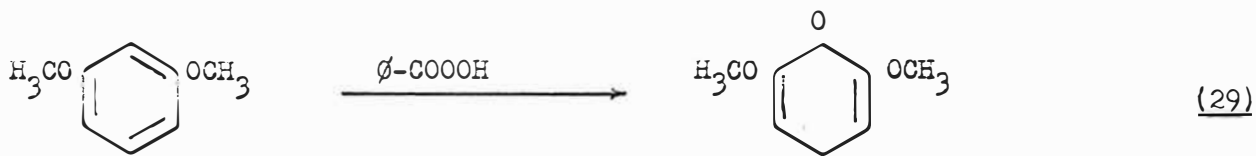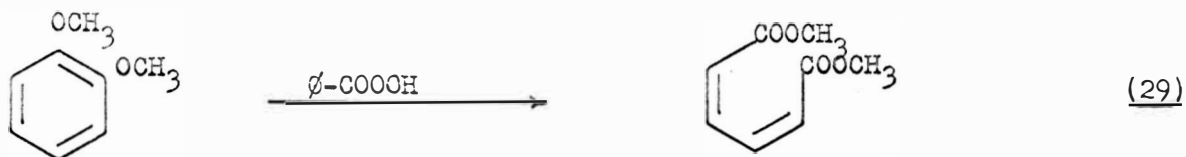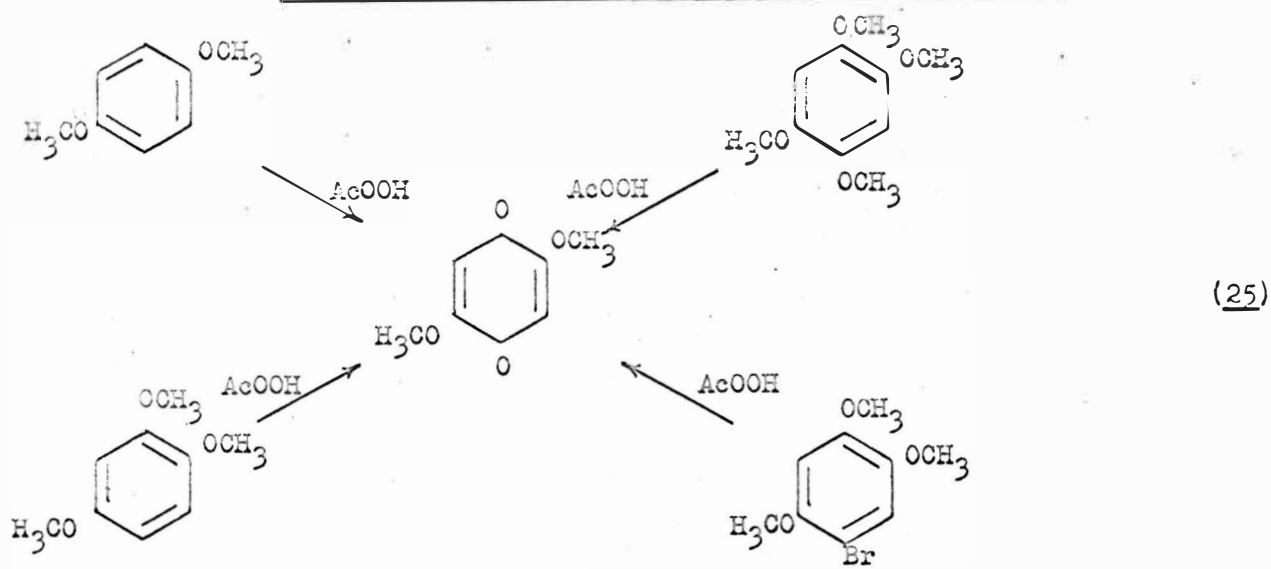
Reactions of Peroxy Acids with Aromatic Compounds

(29)

(29)

No Reaction

(10)

Naphthalene   Phthalic Acid

(10)

(32)

(10)

Phenanthrene   Phenanthrenequinone   Diphenic Acid

(10,19)
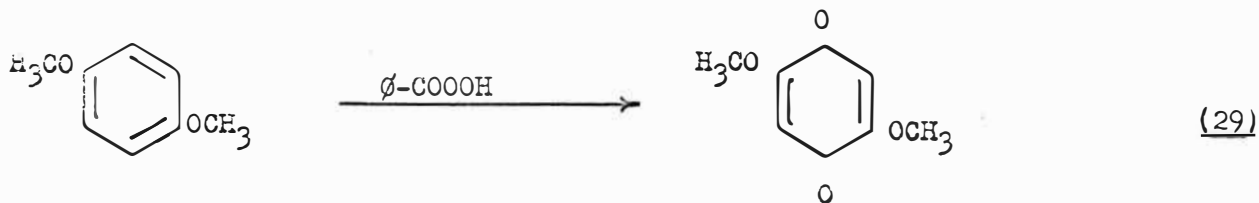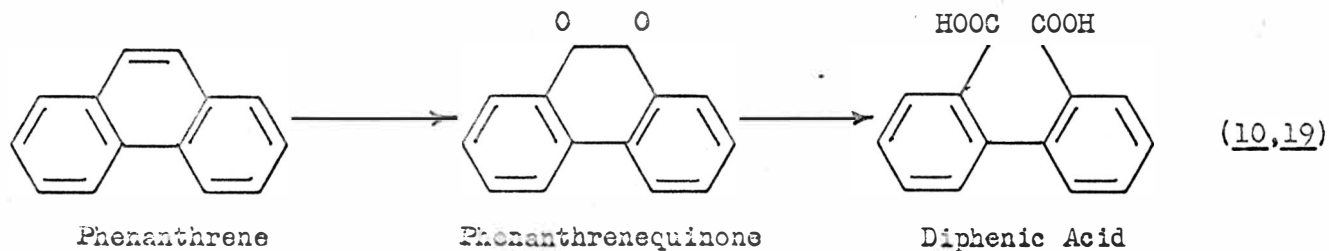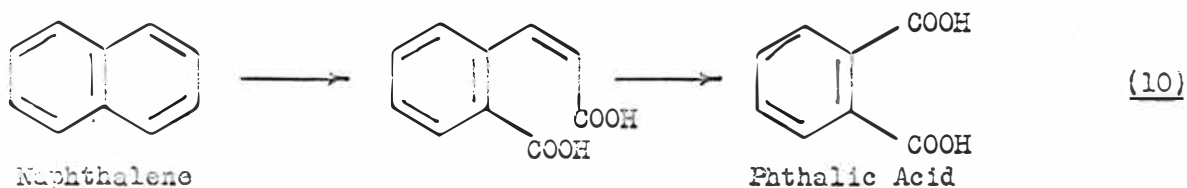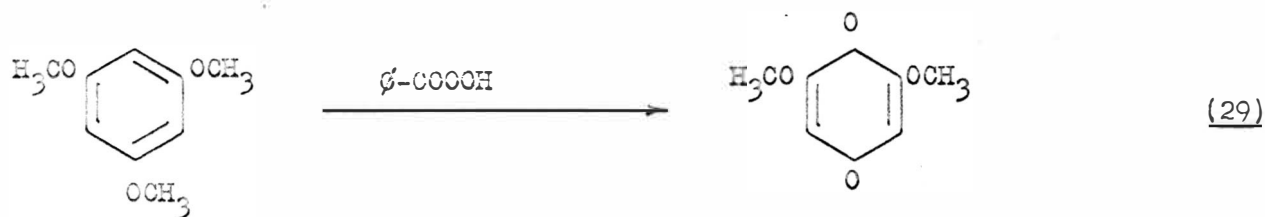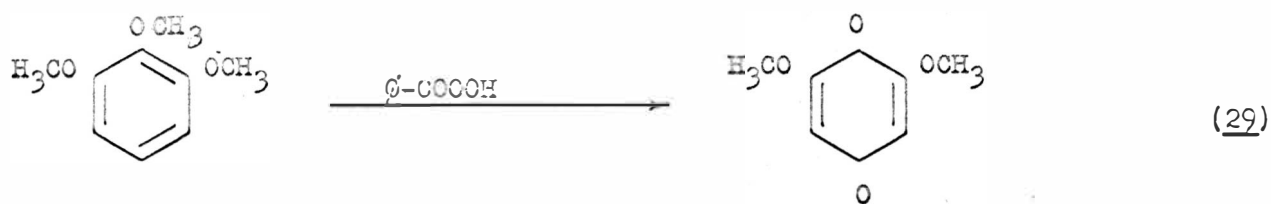
been verified in other works as well. Peracetic acid also reacts with polynuclear, aromatic compounds, yielding both quinones and cleaved ring structures, as summarized in Table I.

EXPERIMENTAL

Since it appeared that the predominant reaction was that of ring cleavage, model compounds were selected which would favor the format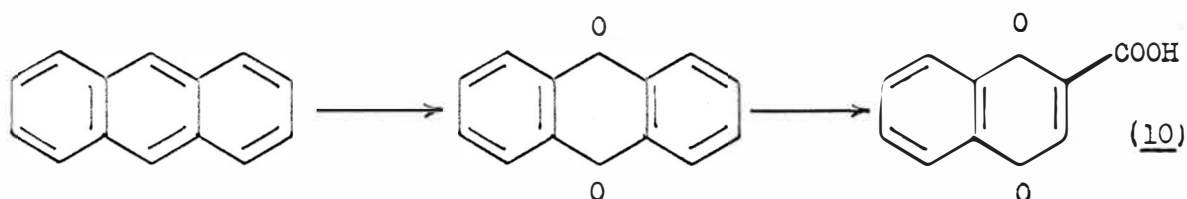ion of open ring structures as major reaction products. Since almost all of the work in the literature was carried out in glacial acetic acid or chloroform, and since it was known that the solvent definitely affects the reaction, it was decided to carry out the reactions in aqueous media, thus more closely simulating actual pulping and bleaching conditions.

The model compounds selected for this study were catechol, guaiacol, and 4-ethylguaiacol. Although the structure of these compounds is not too closely related to lignin, they were selected since, being ortho- disubstituted, they should give the o-benzoquinone intermediates, which would be the most likely to be cleaved.

Reactions in Water Solution

In the first series of reactions, catechol was reacted with a 15% excess of the stoichiometric amount of peracetic acid required to oxidize it to muconic acid. The reaction was carried out at room temperature, in a water bath. The reaction mixture

turned a deep red, characteristic of o-benzoquinone. Upon
standing, no precipitate was observed, which would be expected
for muconic acid, but the reaction mixture became darker.

In additional trials without the water bath, the reaction
flask warmed up considerably, producing foaming, due presumably to
the formation of carbon dioxide, and produced a black precipitate
of carbon.

Reactions carried out in an ice bath, proceeded at a
slower rate, but still yielded the red color, presumed to be
O-benzoquinone. In an attempt to isolate any muconic acid
that might have been formed, it was decided to make the reaction
mixture basic, extract out the quinone with benzene, and then
acidify the aqueous layer. Since muconic acid is insoluble in
water, it should precipitate. However, upon addition of sodium
carbonate, the reaction mixture gradually turned black through
the formation of carbon. The black precipitate was so finely
divided that it was impossible to separate through filtration
or centrifugation. Thus, this extractive method of separation
failed, but demonstrated the pH dependence of the reaction.

A similar series of reactions was carried out with guaiacol.
The reactions proceeded more slowly. However, this could have
been due to the insolubility of guaiacol in water. O-benzo-
quinone was again apparently formed, and upon addition of
sodium carbonate, carbon was formed. Extraction of an original
reaction mixture with benzene, before the addition of base,

separated some of the quinone, but the aqueous layer remained red, and turned black upon addition of sodium carbonate.

It was then decided to extract the black, basic, aqueous reaction mixtures with benzene to remove the quinone present. To overcome a somewhat unfavorable distribution coefficient, a continuous extractor was used, as illustrated in Figure I. This extractor works in the following manner: The solvent, which must be lighter than the solution being extracted, is heated in the larger flask on the right. The vapors condense in the reflux condensor, and fall into the flared neck of the extraction tube. The hydrostatic pressure forces the solvent out through the small holes in the bulb at the bottom of the tube. The solvent then rises through the solution, extracting out the quinones, and returns to the solvent flask. Fresh solvent is regenerated through distillation in the solvent flask, and the volume of solvent required is kept to a minimum. This procedure worked well in removing the highly colored quinones, but upon acidification, no muconic acid was found.

4-ethylguaiacol was oxidized in a similar manner at room temperature. The reaction proceeded very slowly, and neutralization with sodium hydroxide simply salted out unreacted 4-ethylguaiacol with quinone dissolved in it.

Heating the reaction mixtures after they had been allowed to stand for several days made them darken appreciably, but no muconic acid could be filtered from them. At this point it was decided that very little, if any, muconic acid was being formed in aqueous solution.
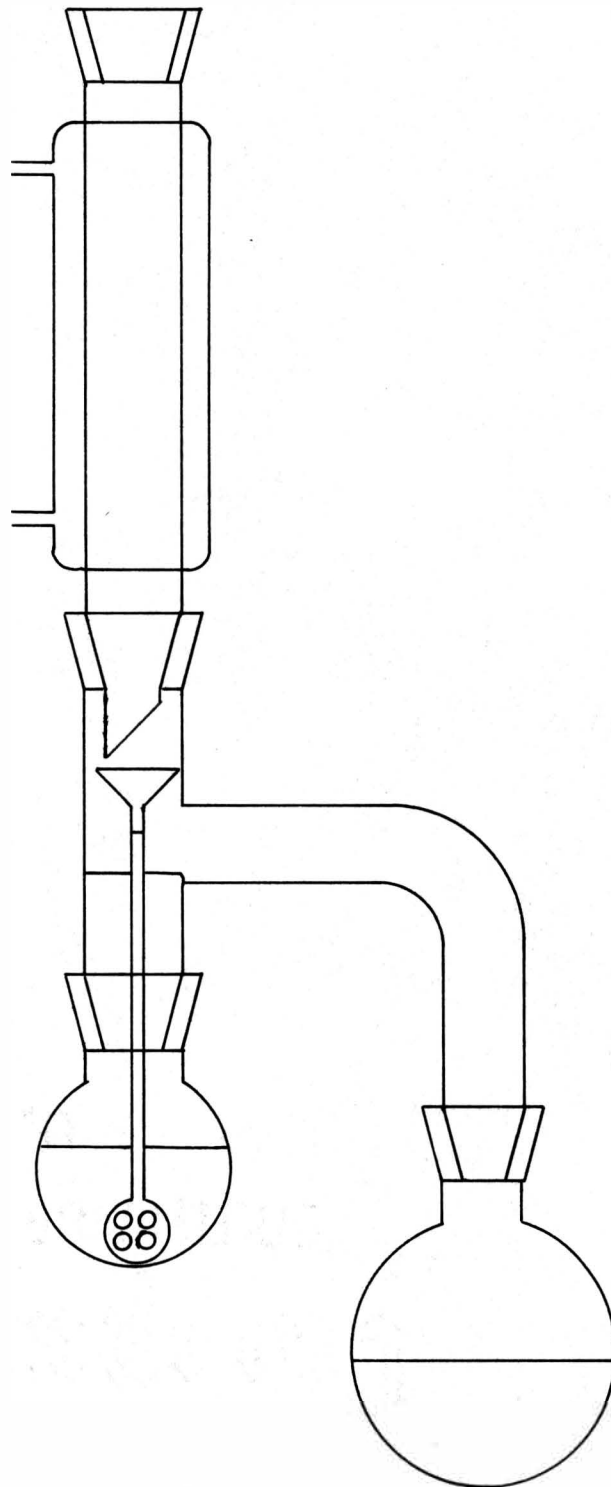
Figure I

Continuous Extractor

Reactions in Ethylene Dichloride

Since it was known that the solvent had a great effect on
these reactions, it was decided to try the reactions in an or-
ganic solvent. In order to do this, the water had to be removed
from the 40% stock solution of peracetic acid. This was done
by taking advantage of an azeotrope formed between ethylene
dichloride and water in a method patented by Korach (31).
The apparatus used is shown in Figure II and operates as follows:
The peracetic acid solution is placed in the large flask on the
right along with the ethylene dichloride, forming two layers.
A vacuum is pulled above the reflux condensor, so that the
ethylene dichloride-water azeotrope will distill at 40 to $45^{o}C$,
well below the explosion point of peracetic acid. The con-
densing azeotrope is retained in the retention chamber for a
certain length of time, during which the mixture cools and
separates into a water layer, and a heavier, organic layer.
The organic layer is returned to the flask, while the top, water
layer is retained. The water can be withdrawn periodically by
opening the stopcock and applying a vacuum to the exit side of
the stopcock. The small funnel prevents the newly condensed
azeotrope mixture from being drawn out when the water is being
removed. The returned solvent forms a new azeotrope, and the
procedure is continued until all the water is removed.

Peracetic acid in aqueous solution is known to exist in
equilibrium, as given by the following reaction:

$$AcOOH \ plus \ H_2O = AcOH \ plus \ H_2O_2$$

to vacuum

to vacuum

H_2O

$C_2H_4Cl_2$
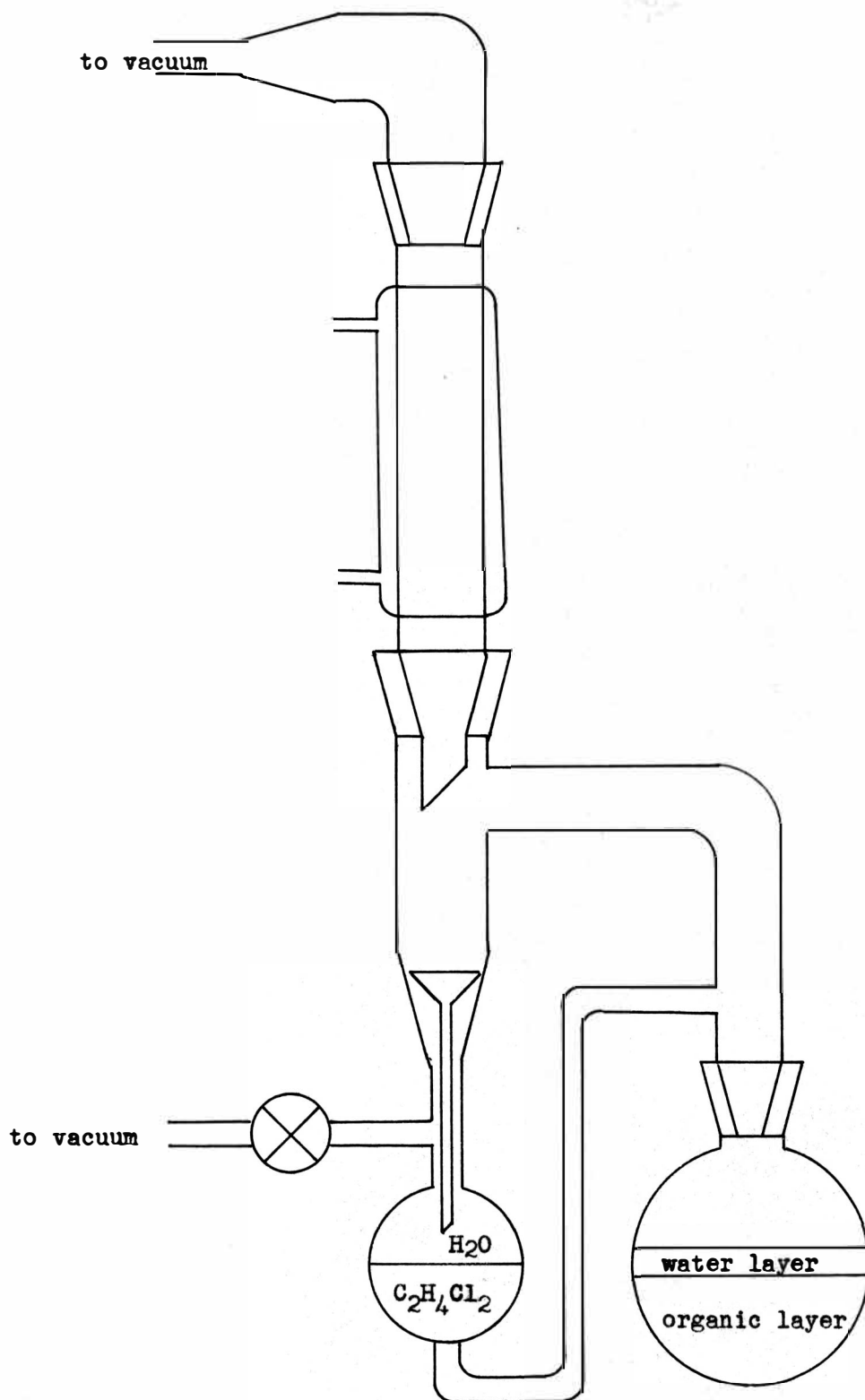
water layer

organic layer

Figure II

Preparation of Peracetic Acid in Ethylene Dichloride

By removing all the water, the equilibrium is shifted entirely to the left, and only peracetic acid is present. Thus, in running these reactions in a non-aqueous medium, all oxidation is due to peracetic acid, and not hydrogen peroxide.

The reactions in ethylene dichloride preceeded much more rapidly than in water, and even when kept in an ice bath, produced carbon dioxide and carbon. The same concentrations were used in both the aqueous and ethylene dichloride reactions. After filtering, the solutions were extracted with aqueous sodium carbonate, after which the water layer turned black, forming a colloidal suspension of carbon.
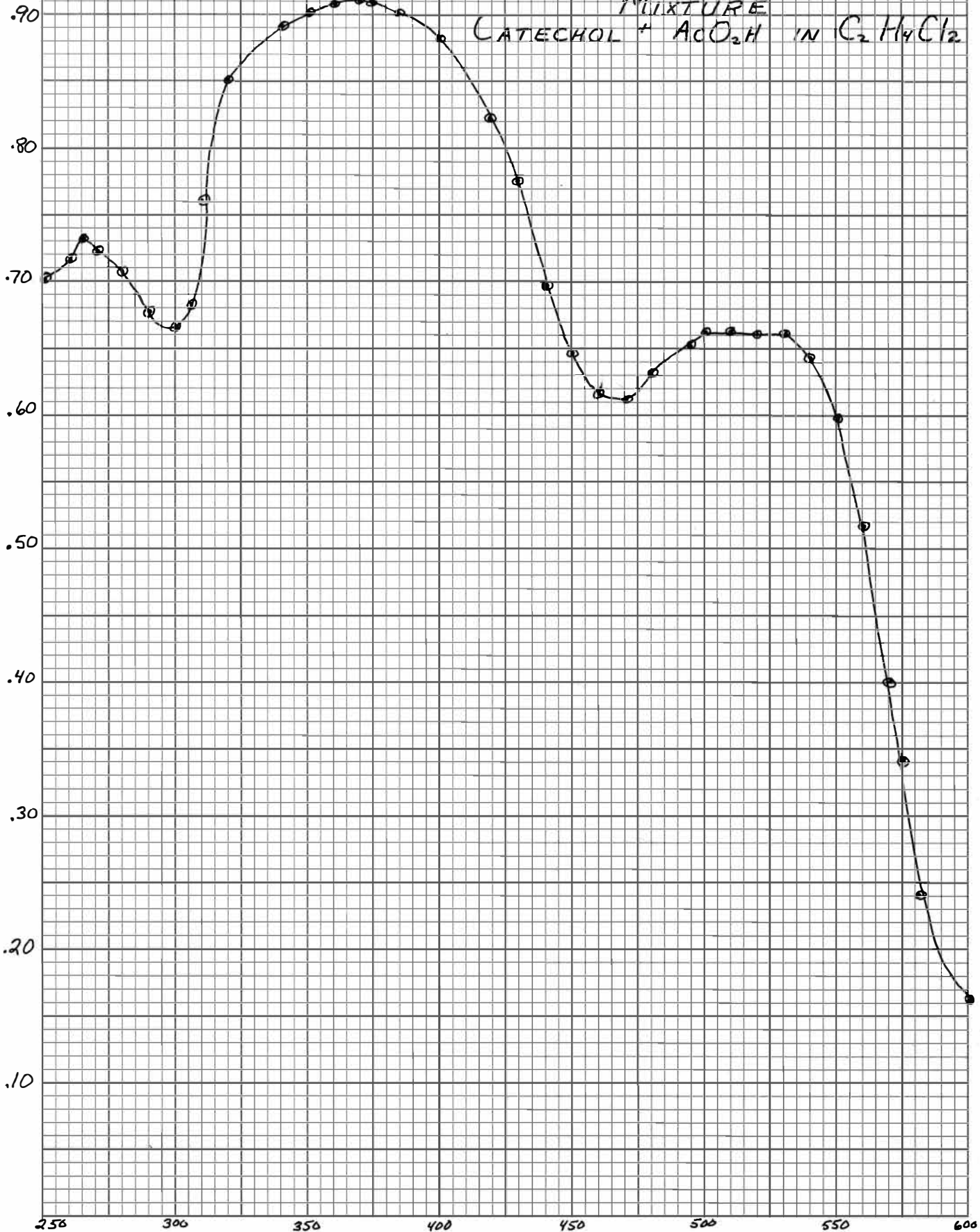
An ultraviolet spectrum on a reaction mixture in which a deficiency of oxidizing agent was added, and which did not turn black, gave a maximum absorption corresponding to that reported for o-benzoquinone.

Since extraction techniques failed to isolate muconic acid, thin layer chromatograms were run on the reaction mixtures; both those which had been run in water and those run in ethylene dichloride. A mixture of 97% chloroform and 7% acetic acid was found to be the best solvent for obtaining a separation. All reaction mixtures produced a spot of identical R_f value, presumably due to O-benzoquinone, since a known spot of trans, trans-muconic acid could not be visualized by phosphorescent dye, iodine vapor, or sulphuric acid. Thus, thin layer chromatography could not be used to prove the presence or absence of muconic acid, but did indicate that at least one compound was present in all reaction mixtures.

Figure III

UV Spectrum of Reaction Mixture

Catechol + AcO_2H in $C_2H_4Cl_2$

Absorbance

Wavelength in mμ.
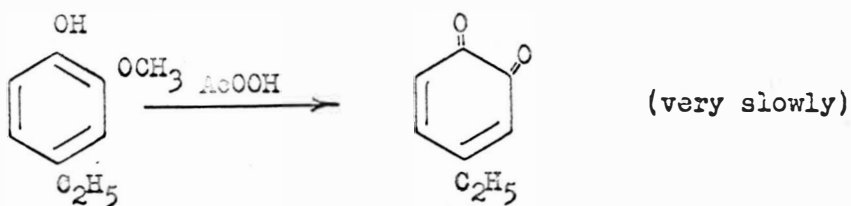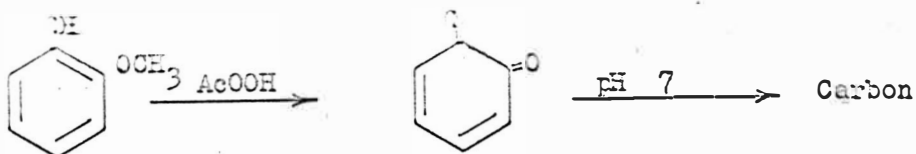
Table II

Reactions Carried Out in Water

$$\text{OH (phenol, OH)} \xrightarrow{\text{AcOOH}} \text{(o-quinone)} \xrightarrow[\text{or heat}]{\text{pH } 7} \text{Carbon}$$

$$\text{(OCH}_3\text{ phenol)} \xrightarrow{\text{AcOOH}} \text{(quinone)} \xrightarrow{\text{pH } 7} \text{Carbon}$$

$$\text{(OH, OCH}_3\text{, C}_2\text{H}_5\text{)} \xrightarrow{\text{AcOOH}} \text{(C}_2\text{H}_5\text{ quinone)} \quad \text{(very slowly)}$$
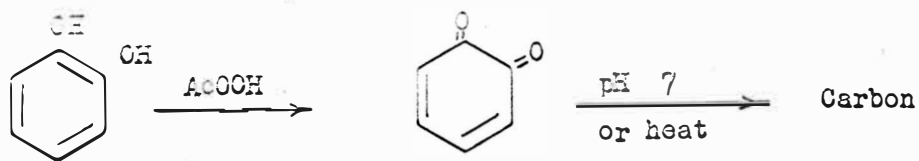
Table III

Reactions Carried Out in $C_2H_4Cl_2$

$$\text{(OH, OH catechol)} \xrightarrow{\text{AcOOH}} \text{(o-quinone)} \longrightarrow \text{Carbon and } CO_2$$

$$\text{(HO, H}_3\text{CO)} \xrightarrow{\text{AcOOH}} \text{(p-quinone)} \longrightarrow \text{Carbon and } CO_2$$
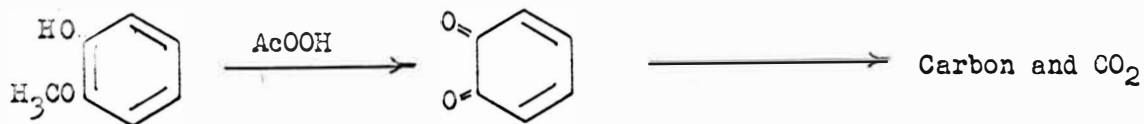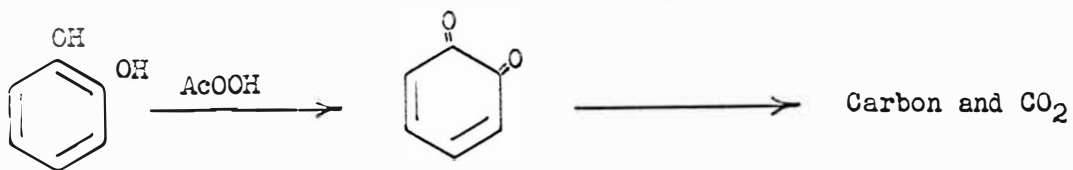
CONCLUSIONS

All efforts to isolate muconic acid failed. Therefore, it is to be concluded that very little, if any, muconic acid is formed in aqueous or ethylene dichloride solutions at the pH ranges studied. However, since the reactions were found to be extremely sensitive to pH and to solvent effects, it is quite possible that it would formed at other pH ranges or in other solvents. The system was found to be much more complex than the literature indicates. In addition to the sensitivity to pH and solvent, temperature and substitution on the aromatic ring was observed to have a profound effect, due both to solubility and chemical reactivity.

Since most of the effort in this study was concentrated on attempting to isolate muconic acid and its derivatives, insufficient work was done in isolation and identification of the quinones which were formed in the reactions. Much more work needs to be done along these lines, including quantitative determination of yields, which would give some idea of the amount of other compounds which might have been formed.

The effect of pH on these reactions must be more thoroughly studied, and reactions with many other model compounds, more closely related to the structure of lignin, must be run in aqueous solvent before definite conclusions can be drawn concerning the reactions of peracetic acid with lignin.

LITERATURE CITED

1. Rapson, W. H., Wayman, M. and Anderson, C. B.,
   Tappi 48(2): 65(1965).

2. Poljak, A., Angew. Chem. A60: 45(1948), C. A. 42:
   17981b (1948).

3. Haas, H., Schoch, W. and Ströle, U., Das Papier
   9: 469-75(1955).

4. Ogait, A., Ger. pat. 969,093 (April 30, 1958),
   C. A. 54: 8082 e (1960).

5. Haney, C. I., Martin, M. E., and Sherk, D. L.,
   U. S. pat. 2,442,332 (June 1, 1948), C. A. 40: 3262 (1946).

6. Poljak, A., Ger. Pat. 1,013,285 (Aug. 8, 1957),
   C. A. 53: 22949a(1959).

7. Bailey, C. W. and Dence, C. W., Tappi 49(2): 9(1966).

8. Wayman, M., Anderson, C. B. and Rapson, W. H.,
   Tappi 48(2): 113(1965).

9. Hackel, J., Kutkiewicz, W. and Kuboszek, R., Przemysl.
   Chem. 43(5):262(1964),

10. Swern, D., Chem. Reviews 45: 1(1949).

11. Koubek, E., Haggett, M. L., Battaglia, C. J. Ibne-
    Rasa, K. M., Pyun, H. Y. and Edwards, J. O., J. Am.
    Chem. Soc. 85(15): 2263(1963).

12. Böeseken, J., Chem. Weekblad 31: 166(1934), C. A.
    28: 1932^8(1934).

13. Böeseken, J., Proc. Acad. Sci. Amsterdam 35: 750-5
    (1932), C. A. 27: 1332 (1933).

14. Böeseken, J., and Engelberts, R., Proc. Acad. Sci.
    Amsterdam 34: 1292(1931), C. A. 26: 2927(1932).

15. Böeseken, J., and Greup, J., Rec. Trav. chim. 58:
    528(1939).

16. Böeseken, J., Lochmann, M. and Konigsfeldt, V.,
    Rec trav. chim. 54: 313(1935), C. A. 29: 3672^6(1935).

17. Böeseken, J., Metz, C. F. and Pluim, J., Rec. trav.
    chim. 54: 345(1935), C. A. 29: 3986^5(1935).

18. Böeseken, J. and Sloof, G., Rec. trav. chim. 49: 91(1930), C. A. 24: 2427(1930).

19. Böeseken, J. and Sloof, G., Rec. trav. Chim. 49: 100(1930), C. A. 24: 2455(1930).

20. Böeseken, J. and Sloof, G., Rec. trav. chim. 32: 1043(1929), C. A. 24: 1085^4(1930).

21. Böeseken, J. and Smitt, L. G., Rec. trav. chim. 58: 125(1939), C. A. 33: 4230^9(1939).

22. Wacek, A., U. S. pat. 2,534,212 (Dec. 19, 1950), C. A. 45: 3415f(1951).

23. Grundmann, C. and Trischmann, H., Ber. 69B: 1755(1936), C. A. 30: 6354^5(1936).

24. Wacek, A. and Fiedler, R., Monatsh. 80: 170(1949), C. A. 44, 3899c(1950).

25. Davidge, H. et al., J. Chem. Soc. 1958: 4569.

26. Sarkanen, K. V. and Suzuki, J., Tappi 48(8): 459(1965).

27. Sarkanen, K. V., Kakehi, K., Murphy, R. A. and White, H., Tappi 45(1): 24(1962).

28. Dence, C. W., Gupta, M. K. and Sarkanen, K. V., Tappi 45(1): 29(1962).

29. Friess, S. L., Soloway, A. H., Morse, B. K. and Ingersoll, W. C., J. Am. Chem. Soc. 74: 1305(1952).

30. Rapson, W. H., Tappi 39 284(1956).

31. Korach, M., U. S. pat. 2,877,266 (March 10, 1959).

32. Fernholz, H., Chem. Ber. 84: 110(1951), C. A. 45: 5123^h(1951).