



Fig. 1. Heating rate: 0—○, 1 deg. C./min.; x—x, 3 deg. C./min.

when the higher heating rate is used.

In this respect there is a close correspondence with the rate of decomposition, the maximum of which is reached at a temperature which is lower the lower the heating rate¹.

This is just another example of the relation between the electron spin resonance phenomena during carbonization, and the classical carbonization phenomena of vitrains².

From this experiment, and from Austen and Ingram's³ work, it is evident that in communications about the numbers of free radicals during carbonization one should report the temperature treatment of the specimen, as this may strongly influence the number of free radicals determined.

J. SMIDT

D. W. VAN KREVELEN

Staatsmijnen in Limburg,
Central Laboratory,
Geleen, Netherlands.

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Colour Reactions of Certain Phenols with Ehrlich's Reagent

THE use of Ehrlich's reagent (1 per cent *p*-dimethylaminobenzaldehyde in *N* hydrochloric acid, for the detection of indoles, pyrroles and related nitrogen-containing compounds has been a long-established analytical procedure^{1,2,3}. Spraying this reagent on paper chromatograms containing indole compounds produces purple, blue, and red spots. However, certain phenols have been reported¹ to produce similar colours under the conditions of the Ehrlich test.

In the course of an investigation of the alkaline degradation products of soil humic acid, we have detected a number of highly coloured spots on paper chromatograms after spraying with Ehrlich's reagent. Flaig⁴, using a degradative procedure identical to ours, obtained similar coloured areas with this reagent and concluded that soil humic acid contains indole-like moieties. Evidence from other investigations in this laboratory (to be reported elsewhere) suggested that some or all of our coloured spots correspond to phenolic compounds, instead of indole-derived compounds.

To test this assumption, we sprayed a number of naturally occurring phenols and phenolic acids with Ehrlich's reagent and with the cinnamaldehyde-hydrochloric acid reagent². The results are tabulated herewith. It is apparent that compounds derived from resorcinol and phloroglucinol react with both reagents. Phloro-glucinol-derived compounds react instantly; resorcinol-derived compounds react more slowly after heating.

The chromatograms were developed in 5 per cent acetic acid-water (v/v) at 24°C. for 3.5 hr. They

were air-dried, sprayed with the colour reagent, air-dried again and placed in an oven for 3 min. at 60°C.

COMPOUNDS WHICH PRODUCED COLOURS

Compound	Colour with Ehrlich's Reagent	Colour with Cinnamaldehyde Reagent	R _F
Phloroglucinol	Cherry red	Dark brown	0.63
Phloroglucinol carboxylic acid	Light pink	Light yellow-brown	0.55
2, 4, 6-trihydroxyacetophenone	Pink	Light brown	0.46
Resorcinol	Purple	Orange-brown	0.73
O-monomethylresorcinol	Purple	Light brown-purple	0.73
O-monoethylresorcinol	Light purple	Light yellow	0.66
O-monoacetylresorcinol	Purple	Light brown	0.58
Oreinol	Light rose	Yellow-brown	0.70
Pyrogallol	Pink	Orange	0.72

COMPOUNDS WHICH DID NOT PRODUCE COLOURS

2-hydroxybenzoic acid	Homophthalic acid
3-hydroxybenzoic acid	Vanillic acid
4-hydroxybenzoic acid	Chlorogenic acid
2, 4-dihydroxybenzoic acid	Quinic acid
2, 6-dihydroxybenzoic acid	Syringic acid
3, 5-dihydroxybenzoic acid	Catechol
Gentisic acid	Tolhydroquinone
Homogentisic acid	Galic acid

CORNELIUS STEELINK

Department of Chemistry,
University of Arizona,
Tucson, Arizona.

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Oxidation of Ethyl Alcohol by a Mixture of Hydrogen Peroxide and Ferric Salts

It was recently found that the catalytic decomposition of hydrogen peroxide by ferric ions, and by enzymes containing haemin groups follow closely related paths¹. This analogy can be extended to the oxidation of ethanol by a mixture of hydrogen peroxide and ferric salts. The experimental data of Walton and Christensen² provide evidence that ethanol is oxidized by the secondary hydrogen peroxide-ferric ion complex. A similar mechanism for peroxidase action was derived by Chance³.

Walton and Christensen observed that the rate of oxidation of alcohol at high $[H_2O_2]/[Fe^{3+}]$ ratios becomes:

$$\frac{d[C_2H_5OH]}{dt} = k[C_2H_5OH]$$

where k is proportional to $[Fe^{3+}]_t$ (total concentration of ferric ions) and independent of $[H_2O_2]$.

Regarding the steady-state concentrations of the two intermediate complexes observed during the catalytic decomposition of hydrogen peroxide (equations X a and X b in ref. 1) it is seen that in the range where $[H_2O_2] \ll K_M + (k_3/k_4)$ (this is the case when $[H_2O_2]$ is some tenths of a mole per litre at a pH not exceeding 2):

$$[C_I] \sim [Fe^{3+}]_t [H_2O_2], \text{ whilst } [C_{II}] \sim [Fe^{3+}]_t.$$

Thus, the observed rate law can be obtained only if ethanol reacts with the secondary complex.

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MORDECHAI L. KREMER

Weizmann Institute of Science,
Isotope Department,
Rehovoth, Israel.

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