

where Q^* is the coupling coefficient, H is the vacancy formation energy, R is the gas constant, T and T_0 are respectively the highest attained temperature and the temperature near the boundary of the circular region over which the temperature gradient is superimposed.

Substituting the values of the above parameters applicable to the present case,^{1,6} $Q^* - H = 0.1$ eV, $T = 1100^\circ\text{C}$, $T_0 = 300^\circ\text{C}$, we find that $c/c_0 \approx 39$. This is much greater than the value of about 10^{-3} which is thought to be necessary for helix and loop formation in bulk specimens.^{3,4} In the present case, since the specimen is in the thin film form, as is well known, a large portion of the vacancy population will go to surfaces. However, even if a small part of the vacancy population goes to interact with the dislocations, the formation of helices and the consequent loops will take place.

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OXIDIMETRIC DETERMINATION OF PHLOROGLUCINOL

THOUGH cerium(IV) salts in sulphuric and perchloric acid media have been extensively employed in the oxidimetric determination of organic compounds, the oxidation of phloroglucinol has not yet been investigated. Since hydroquinone containing two hydroxy groups is oxidized instantaneously to quinone with ceric sulphate it was considered interesting to study the oxidation of phloroglucinol containing three hydroxy groups with the same reagent. Phloroglucinol occurs as a constituent of many resins and is a useful starting material in the synthesis of naturally occurring flavone and flavanol pigments.

Reagents: *Ceric sulphate*.—The requisite amount of ceric ammonium sulphate (B.D.H.) is made into a paste with concentrated sulphuric acid, warmed, dissolved in distilled water and made up to one litre. Final normality of sulphuric acid is one and that of

cerium(IV) ≈ 0.100 . This solution is standardised employing the usual methods. *Phloroglucinol* (Rideal de Haen) was dissolved in distilled water to give a 0.010 molar solution of the compound. *N-phenyl anthranilic acid* solution is prepared by dissolving 0.1 gm. of the acid along with 0.1 gm. of sodium carbonate in 100 ml. distilled water.

Ferrous ammonium sulphate.—B.D.H. AnalaR ferrous ammonium sulphate was employed in preparing 0.05 M Fe(II) solution in one molar sulphuric acid. The solution was standardised everyday with standard potassium dichromate solution. All other reagents used were of standard and tested purity.

To a measured aliquot of phloroglucinol solution taken in a 250 ml. Erlenmeyer flask a known excess of ceric sulphate solution is added. Sufficient amount of sulphuric acid is added to bring the acid normality to the desired level and the volume made up to 75 ml. The solution was heated on a water-bath, and after cooling the excess cerium(IV) remaining in the solution is titrated with Mohr's salt solution using *N-phenyl anthranilic acid* as indicator. The effect of the following variables was investigated:

(1) Effect of acidity; (2) Effect of time of heating; (3) Effect of excess cerium(IV). In all cases blanks were run and suitable blank corrections applied to the final titre value.

From a study of the different variables it was found that heating for 30 minutes on water-bath in presence of one molar sulphuric acid employing a minimum of 30-fold excess cerium(IV) gave the best possible results. The results given in Table I employing dif-

TABLE I

Oxidation of phloroglucinol with ceric sulphate

Phloroglucinol milli-moles taken	0.010	0.020	0.030	0.040
Cerium (IV) milli-moles consumed	0.241	0.480	0.723	0.960
No. of moles of cerium (IV) consumed per mole of phloroglucinol	24.1	24.0	24.1	24.0

ferent amounts of phloroglucinol under these conditions indicate that 24 equivalents of cerium(IV) are utilised in the oxidation of each mole of the compound. For the complete oxidation of phloroglucinol to carbon dioxide and water according to the equation

$\text{C}_6\text{H}_6\text{O}_3 + 9\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 24\text{H}^+ + 24\text{e}^-$,
each mole of phloroglucinol requires 24 moles of

one electron oxidant such as cerium(IV). Hence it may be concluded that under the above conditions oxidation of phloroglucinol goes to completion giving carbon dioxide and water as final products. The evolution of carbon dioxide during the oxidation has been tested qualitatively. The oxidation seems to proceed *via* a free radical intermediate as in the case of oxidation of several other organic compounds with cerium(IV) in sulphuric acid solution.² Here also acrylo-nitrile test indicated the presence of free radical in the reaction mixture. The results also indicate that phloroglucinol can be estimated volumetrically under the prescribed conditions employing ceric sulphate.

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THERMAL DECARBOXYLATION OF SUBSTITUTED CHLOROBENZOIC ACIDS

THERMAL decarboxylation studies on salicylic and chlorobenzoic² acids in solvents glycerol and resorcinol have shown that when *ortho*, *para* directing substituents are present in *ortho* or *para* position to the carboxylic group, the reaction proceeds by an S_E2 mechanism. The kinetic investigation of Sastry *et al.*³ on 3-nitro and 3,5-dinitro salicylic acid also indicated that the introduction of a nitro group in 3- and 3,5-positions decreased the rates and energies of activation of salicylic acid in resorcinol though following the same S_E2 mechanism. The decrease in rate constants and other thermodynamic parameters were attributed to the deactivating influence of the nitro group. In view of the above studies, thermal decarboxylation of nitro-substituted chlorobenzoic acids have been carried out in neutral solvent, glycerol and the results are presented in Table I. The apparatus used and method employed for following the rates were same as those given in our earlier paper.⁴

From our recent investigations, it was concluded that *m*- and *p*-nitrobenzoic acids follow an S_E1 mechanism, in which the cleavage of the C-C bond between carboxyl carbon and

the carbon atom of the ring is the rate-determining step. The 3- and 4-nitrochlorobenzoic acids were found to be stable in resorcinol unlike nitro-salicylic acids and showed higher rates than the corresponding *o*- and *p*-unsubstituted chlorobenzoic acids and even more than *m*- and *p*-nitrobenzoic acids in glycerol. Hence, it is concluded that these acids, unlike simple chlorobenzoic acids, follow an S_E1 mechanism. This was further confirmed by studying the effect of boric acid on the rate constants which decreased with increase of boric acid concentration in glycerol. The change in mechanism from S_E2 to S_E1 for the chloro and nitro-substituted chlorobenzoic acids may be explained as follows.

From the dissociation constants of aromatic halogeno acids, it was concluded that the inductive effect of the halogens becomes the predominant factor and deactivates the ring, although it is superimposed by the mesomeric effect in many electrophilic substitution reactions.⁵ Further it was observed that the acid strength is enhanced by introducing a *meta* orienting substituent in 3-position. Thus, the inductive effect of the chlorine group and the inductive and mesomeric effects of the nitro group together deactivates the ring and thus facilitates—C-C bond cleavage resulting in high rates of decarboxylation.

TABLE I

Kinetic data on the thermal decarboxylation of nitro-chlorobenzoic acids in glycerol in the temperature range 200–250° C.

Acid	$K \times 10^4$	$k \times 10^4$ SEC. ⁻¹	ΔE^* k.cals.	ΔH^* k.cals.	ΔF^* k.cals.	ΔS^* e.u.
<i>o</i> -Chloro ² ..	11.97	2.7	39.6	38.6	37.1	+ 0.56
<i>p</i> -Chloro ² ..	1.04	3.5	40.6	39.6	37.9	+ 3.39
<i>m</i> -Nitro ⁴ ..	3.35	20.0	17.7	16.7	37.4	-39.00
<i>p</i> -Nitro ⁴ ..	3.70	22.5	17.5	16.5	37.2	-39.10
4-Chloro-3-nitro	4.60	28.1	28.3	27.3	36.7	-17.10
2-Chloro-3-nitro	87.00	53.4	19.3	18.3	36.4	-33.80
2-Chloro-4-nitro	103.00	52.4	20.1	19.1	35.3	-32.24

From a study of dipole moments and interatomic distances Jenkins⁶ has concluded that as the distance between the substituent and the carboxyl group decreases, the influence of the inductive effect overweighs the mesomeric effect in isomeric halogeno acids. The high rates of decarboxylation of 2-chloro and 2-chloro-4-nitro, 3-nitrobenzoic acids as compared to 4-chloro, 3-nitrobenzoic acid observed