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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Indian Institute of D. O. SHAH.
Technology,
New Delhi-29, *May* 30, 1970.

1. Kolthoff. I. M. and Belcher, R., *Volumetric Analysis*, Vol. III, Interscience Pub., New York, 1957.
2. *Oxidation in Organic Chemistry*, Edited by Wiberg, K. W., Interscience Pub., New York, 1965.

THERMAL DECARBOXYLATION OF SUBSTITUTED CHLOROBENZOIC ACIDS

THERMAL decarboxylation studies on salicylic[1] and chlorobenzoic[2] 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.
o-Chloro[2] ..	11·97	2·7	39·6	38·6	37·1	− 0·56
p Chloro[2] ..	1·04	3·5	40·6	39·6	37·9	− 3·39
m-Nitro[4] ..	3·35	20·0	17·7	16·7	37·4	−39·00
p-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	36·3	−32·24

From a study of dipole moments and interatomic distances Jenkins[6] 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

in the present investigation supports Jenkin's view. From the knowledge of ionisation constants of 2-chloro-3-nitro and 2-chloro-4-nitrobenzoic acids it is likely that the former should have a low rate compared to its *ortho* isomer. However, from the experimental observation it is found that 2-chloro-3-nitrobenzoic acid decarboxylates at a higher rate than 2-chloro-4-nitrobenzoic acid. This is due to the fact that the halogen atom in the 2-chloro-3-nitrobenzoic acid is bent out of the plane of the ring by the large groups on either side of it and thus is prevented from attaining the planar configuration necessary for the mesomeric effect. Since, the nitro group is *para* to carboxyl group, in 2-chloro-4-nitrobenzoic acid, such a steric effect is improbable and results in a low rate. A comparison of the enthalpies and entropies of activation of the two isomers is a further evidence for the proposed S_E1 mechanism. Although the inductive effect of the chlorine is the predominant factor, it is superimposed by the mesomeric effect to a greater extent in 4-chloro-3-nitrobenzoic acid. The net effect arising from the combination of these two increases the C–C bond strength and results in higher enthalpy of activation than its *ortho* isomer. This seems to be the reason for the low rate observed in the 4-chloro-3-nitrobenzoic acid.

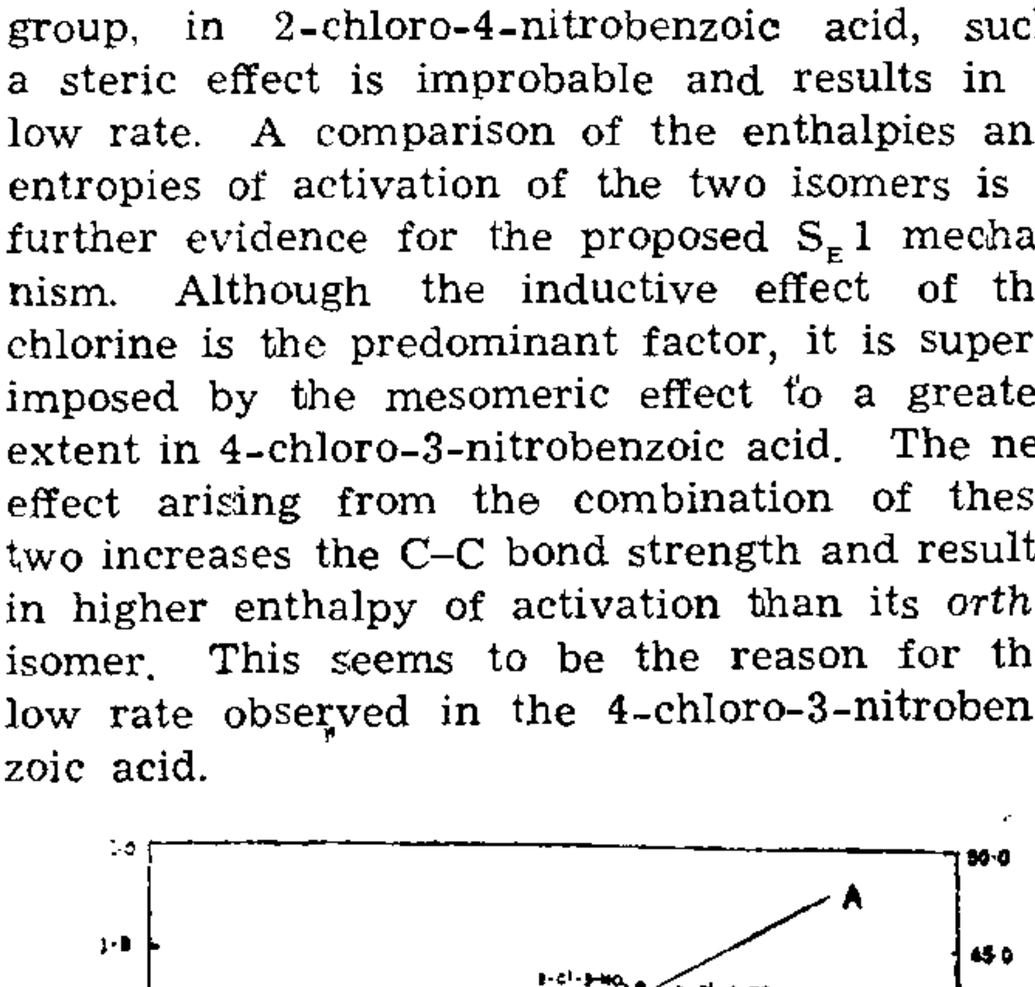

FIG. 1. A, Plot of log *k vs.* log K ; B, Plot of H^* *vs.* S^*.

The plot of log *k* against log K gave a linear relationship as in Fig. 1, A with a slope of + 0·27 suggesting that the decarboxylation is facilitated by electron withdrawing groups, a characteristic of the S_E1 mechanism.[8] The other plot, Fig. 1, B, ΔH^* against ΔS^* also reveals that all these acids follow a similar mechanism except *o*- and *p*-chlorobenzoic acids and the isokinetic temperature is calculated as 509° K.

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E. V. SUNDARAM.

1. Brown, B. R., Hammick, D. H. LL. and Scholefield, A. J. B., *J. Chem. Soc.*, 1950, p. 778.
2. Muhammad, S. S. and Aziz Siddiqui, *Thesis*, approved by Osmania University, 1957.
3. Sastry, K. S., Sundaram, E. V. and Muhammad, S. S., *Curr. Sci.*, 1968, **37**, 643.
4. Sita Manikyam, D. and Sundaram, E. V., *Bull. Chem. Soc., Japan* (In press).
5. Dippy, J. F. J., *Chem. Revs.*, 1939, **25**, 150.
6. Jenkins, H. O., *J. Chem. Soc.*, 1939, p. 640.
7. Hammett, L. P., *Physical Organic Chemistry*, McGraw-Hill Co., New York, 1940, p. 184.
8. Brown, B. R., *Quart. Revs.*, 1951, **5**, 131.
9. Clark, L. W., *J. Phys. Chem.*, 1956, **60**, 1340; 1958, **62**, 70.

2-SUBSTITUTED AMINOPROPIONAMIDOXIMES AND THEIR DERIVATIVES

AMINOACETAMIDOXIMES, having alkyl or aryl substituents on the nitrogen, have been reported[1] to possess fungicidal properties. 2-Arylaminopropionic acids and their amides have been claimed[2] to possess antidiabetic activity. So, the synthesis of 2-substituted aminopropionamidoximes and their carbamate derivatives was undertaken.

The 2-substituted aminopropionitriles required for our work were prepared by standard literature methods.[3] The nitriles were converted to the corresponding amidoximes in 40–60% yields by reacting them with hydroxylamine in aqueous ethanol. The oximes, on reaction with potassium cyanate, gave their O-aminocarbonyl derivatives. Compounds 4, 7 and 11 (Table I) have shown significant oral hypoglycemic properties, but they have also been toxic.

2 - o - Chloroanilinopropionamidoxime.—2 - o - Chloroanilinopropionitrile (4·5 g. ; 0·025 mole), hydroxylamine hydrochloride (1·75 g. ; 0·025 mole) and potassium carbonate (1·75 g. ; 0·013 mole) were refluxed in 80% ethanol (100 ml.) for 5 hours. The solvent was removed *in vacuo* ; the gummy residue was washed with ice-cold water and then chromatographed over