The Photoinduced Decarboxylation of *N*-(2-Chlorophenyl)glycine and (Phenylthio)acetic acid Sensitised by Aromatic Nitro-compounds

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Summary Aromatic nitro-compounds photosensitise the decarboxylation of *N*-(2-chlorophenyl)glycine to give 2-chloroaniline, and of (phenylthio)acetic to give thiophenol and methyl phenyl sulphide, excited charge-transfer complexes are suggested as intermediates

THE mechanism of the photoinduced decarboxylation of substituted *N*-(2-nitrophenyl)glycines[1] and 2-nitrophenoxyacetic acids[2] has been the subject of recent debate [3] The finding that *N*-(4-nitrophenyl)valine undergoes decarboxylation on irradiation[4] is indicative that this type of reaction can occur *via* an intermolecular mechanism This suggestion has now been verified by the finding that irradiation of acetonitrile solutions of aromatic nitro-compounds containing *N*-(2-chlorophenyl)glycine, and also (phenylthio)acetic acid causes decarboxylation

The Table shows the products and their yields, obtained from some of the decarboxylation reactions studied It is most unlikely that these reactions are occurring *via* a mechanism which involves hydrogen atom abstraction by the excited nitro-compounds since the two reactive compounds, 1-nitronaphthalene and 4-nitrobiphenyl, have lowest triplet states of a $\pi\pi^*$ configuration[5] which are known to be ineffective hydrogen atom abstractors We therefore suggest, by analogy to the mechanism proposed for the decarboxylation of carboxylic acids sensitised by ketones and quinones,[6] that the reactions occur *via* excited charge transfer complexes [*e g* (I)] These complexes can collapse to give carbon dioxide and radicals by intramolecular transfer of a proton

Products obtained by irradiation[a] *of* N-(2 *chlorophenyl)glycine and (phenylthio)acetic acid in the presence of aromatic nitro compound*

	N-(2-Chlorophenyl)glycine			(Phenylthio)acetic acid			
Aromatic nitro-compound	Carbon dioxide %	2 Chloroaniline %	Nitro compound utilised %	Carbon dioxide %	Methyl phenyl sulphide %	Thiophenol %	Nitro-compound utilised %
1 Nitronaphthalene	65	37	41	29	*ca* 5	*ca* 4	12
4-Nitrobiphenyl	68	40	37	49	*ca* 7	14	39
1 3-Dinitrobenzene	60	40	28				
4 Methylnitrobenzene	67	50	26				
Nitrobenzene	37	21	19				

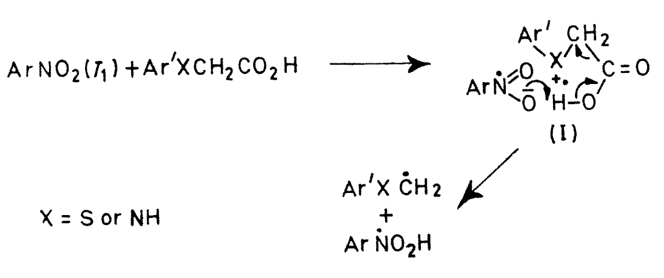
[a] Irradiations carried out with a Rayonet reactor equipped with fluorescent tubes having maximum emission at 310 nm

The recently reported positive evidence for excited charge-transfer complex formation between aromatic nitro-compounds and amines[7] as well as aromatic hydrocarbons[8] lends credence to the suggested mechanism

The formation of 2-chloroaniline from *N*-(2-chlorophenyl)-glycine and of thiophenol from (phenylthio)acetic acid is rationalised on the basis of the following oxygen transfer reaction Hydrolysis of the hemiacetal produced in this reaction gives the observed products Crystalline products derived from the nitro-compounds have not, as yet, been isolated In the case of the reaction with the glycine, many highly coloured products are formed and it is thought that these are azo-compounds, produced by the condensation of the nitroso-compound with the aniline

$$\mathrm{Ar\overset{+\bullet}{N}{-}OH \quad \overset{\bullet}{C}H_2XAr \longrightarrow ArN{=}O + ArXCH_2OH}$$

x = NH or S



We thank the S R C for a maintenance grant (P R S)

(*Received, June 30th,* 1971, *Com* 1097)

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