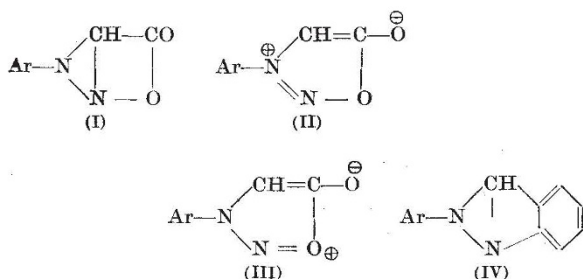


LETTERS TO THE EDITORS

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Structure of the 'Sydneses'

It has been shown by J. C. Earl¹ that the N-nitroso-N-arylglycines, for example, Ph.N(NO).CH₂.CO₂H, on treatment with acetic anhydride lose a molecule of water, giving monomolecular anhydro derivatives which have been termed 'sydneses'. The structure tentatively suggested for these compounds contains the fused three- and four-membered ring system (I), and is unacceptable for a number of reasons which need not be enumerated.



As shown by Earl, the 'sydneses' are converted into the original N-nitroso-N-arylglycines by hydrolysis with alkali, and it is therefore most improbable that any molecular rearrangement, such as migration of the aryl group, occurs during their formation. The five-membered ring system shown in (I) is, therefore, almost certainly present in the 'sydneses'. A modification of the structure proposed by Earl, however, avoids the obvious difficulties inherent in the formulation (I); it also allows a ready explanation of the stability of the compounds and accounts equally satisfactorily for their properties. The modification now advanced omits the bridge bond in (I), and substitutes a hybrid structure derived from a number of ionic states of which there are, for example, eight zwitterionic forms (not all of equal probability), two of which are shown in formulae (II) and (III). On this view the 'sydneses' are partially aromatic in character, and might be expected to possess the degree of stability which they, in fact, show.

The problem of the structure of the 'sydneses' is closely related to that of the 2-substituted indazoles (IV; shown with a bridge bond to compare with I) and related compounds such as anthranil, 2-substituted benzotriazoles, etc., for which a hybrid, largely zwitterionic structure has already been advanced by one of us². Work on the structure of this type of molecule and on the 'sydneses' is in progress, and a full report will be published elsewhere.

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¹ Earl, J. C., and Mackney, A. W., *J. Chem. Soc.*, 899 (1935). Earl, J. C., and Eade, R. A., *J. Chem. Soc.*, 591 (1946).

² Baker, W., Tilden Lecture, *J. Chem. Soc.*, 267 (1945).

Catalytic Oxidation of Ascorbic Acid

BARRON *et al.*¹ showed that ascorbic acid is not autoxidizable in acid solutions up to pH 7. They investigated the catalytic effect of salts of manganese, nickel, iron, cobalt, calcium and copper at pH 4-6 and found that copper alone had a marked catalytic effect. Mack and Kertesz² found that iron had no catalytic effect alone but increased the catalytic effect of copper.

Investigations in this Laboratory have shown that catalysis by ferrous iron is negligible above pH 2 but considerable at pH 1 and below. In contrast, copper catalysis decreases with decreasing pH and becomes negligible below pH 1. The accompanying table shows results of studies in solutions of 0.1 M sodium acetate adjusted to various pH levels with sulphuric acid. The solutions contained initially 20 mgm. of ascorbic acid per 100 ml. and were aerated rapidly at 40° C.

Catalyst added	Per cent oxidation in 5 min. at pH			
	0.4	1.0	2.0	3.0
Nil	0	0	0	0
Cu ⁺ (10 p.p.m.)	0	0.3	7.0	54.3
Fe ⁺ (10 p.p.m.)	43.0	20.8	0.9	0.9

At pH 0.4, copper has practically no catalytic effect but actually reduces the catalytic effect of iron. These results, in addition to their theoretical interest, are of importance in relation to the determination of ascorbic acid in canned foods. Further details will be published later.

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¹ Barron, E. S. G., *et al.*, *J. Biol. Chem.*, 112, 625 (1936).

² Mack, G. L., and Kertesz, Z. I., *Food Res.*, 1, 377 (1936).

A Direct Method for Determining the Index of Refraction of Thin Films

IN working with high-frequency discharges obtained in air, at a pressure of about 1 mm., by the use of external electrodes surrounding a glass tube, an interference pattern was observed after a run of twenty hours or more. The pattern was visible both inside the tube at the edges of the electrodes and on glass strips placed under the electrodes within the tube. Patterns were obtained on clear strips of glass and on strips previously coated with thin metallic layers. Fig. 1, an enlarged photograph taken by sodium light reflected from the surface of a strip, shows a characteristic pattern which was formed on that portion of the strip immediately under one of the electrodes. The pattern appears to be similar in nature to those observed by Bochstahler and Overbeck¹, Nathanson², Nathanson and Bartberger³ and others, in sputtering discharges, and is due apparently either to the deposition of a thin layer



Fig. 1