

will be the case if the termination process is the reaction of the positive ionic active centre with a negative charge as suggested by Polanyi⁵. (The rate of reaction between ions of opposite sign is reduced by increase in dielectric constant⁷.)

Quantitatively, the equations developed by Eyring and his co-workers⁷ for the reaction between two ions do not fit the above data. Perhaps, in view of the composite nature of the overall rate, this is not to be expected. Qualitatively, the results are in agreement with the theory that the dielectric nature of the medium acts mainly by influencing the termination rate, that is, the rate of destruction of ionic-growing chain centres.

No account has been taken of possible chain transfer processes, since they affect the degree of polymerization rather than the rate⁸, and hence are unlikely to be important here. This is in marked contrast to the radical polymerization of styrene, where the influence of different solvents is attributed⁸ entirely to their different transfer constants.

The polymerizations were followed, and the molecular weight of the products measured, by bromination. Full experimental details will be published later.

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¹ Staudinger, H., and Breusch, F., *Ber.*, **62**, 442 (1929).

² Hershberger, A. B., *et al.*, *Ind. Eng. Chem.*, **37**, 1073 (1945).

³ Whitmore, F. C., *Ind. Eng. Chem.*, **26**, 94 (1934).

⁴ Price, C. C., *N.Y. Acad. Sci.*, **44**, 351 (1943).

⁵ Polanyi, M., *Chem. Soc. Symposium*, see *Nature*, **158**, 223 (1946).

⁶ Kirkwood, J. G., *J. Chem. Phys.*, **2**, 351 (1934).

⁷ Glasstone, Laidler and Eyring, "Theory of Rate Processes", 419 *et seq.* (McGraw-Hill, 1941).

⁸ Mayo, F. R., *J. Amer. Chem. Soc.*, **65**, 2324 (1943).

Cis-Trans Isomerism of Diethylstilbœstrol

Walton and Brownlee¹ have reported the conversion of pure ψ -diethylstilbœstrol (*cis* ?) into diethylstilbœstrol (*trans*) in 80 per cent yield by heating with alcoholic hydrochloric acid. Recent work in this laboratory has shown that heating with 2.5 *N* aqueous hydrochloric acid for periods of 30 min.–2 hr. converts both ψ -diethylstilbœstrol and diethylstilbœstrol into an equilibrium mixture in which, in so far as these two substances are concerned, diethylstilbœstrol preponderates in the ratio 9 : 1. The change has been followed by melting-point and colorimetric estimations² of the products isolated from saturated acid solutions after cooling to room temperature, and checked by comparison with the properties of suitable mechanical mixtures.

It would seem, however, that a simple binary equilibrium is not involved, and that at least one other—and presumably a more soluble and less chromogenic—substance is implicated. This may be deduced from the fact that the theoretical intensity of colour which might be expected from a 9 : 1 proportionality of the two substances is not attained in experiments involving quantitative recovery by ether extraction, and from the stability of the system over the period studied, which would seem to preclude any progressive change in the equilibrium conditions due to the gradual removal or destruction of one of the components.

The further possibility that the 9 : 1 proportionality in the solid phase may not reflect the true equilibrium ratio in the saturated liquid owing to differences in the solubilities of the *trans*- and ψ -forms, and that this ratio might be more nearly 1 : 1, which would very simply account for the low colour development, is not supported by preliminary experiments; these show that both substances are only very slightly soluble in acid solution at room temperature and, in fact, suggest a slightly greater solubility for the *trans* form.

Estrogen	Duration of acid treatment (min.)	Product m.pt. °C. (uncorr.)	Chromogenic power*[%C]	Recovery % theoretical chromogenic power [%C]
Diethylstilbœstrol	0	171	100	98
"	30	157	94.5	79
"	90	158.5	96	80
ψ -Diethylstilbœstrol	0	149.5	56.5	104
"	30	157	96	75
"	90	157.5	95	76
Mechanical mixture†	—	159.5	95	100

* Expressed as a percentage pure diethylstilbœstrol colour intensity.

† Diethylstilbœstrol : ψ -diethylstilbœstrol = 9 : 1.

Typical results are summarized in the accompanying table; they are clearly of importance in the chemical estimation or biological assay of conjugated forms of diethylstilbœstrol after acid hydrolysis.

Hexœstrol has been found to be quite stable under similar conditions of acid treatment, and to yield quantitative recoveries.

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¹ Walton, E., and Brownlee, G., *Nature*, **151**, 305 (1943).

² Malpress, F. H., *Biochem. J.*, **39**, 95 (1945).

Metallo-organic Complexes in Soil

Dion and Mann¹ have shown that, as extractants for manganese from soil, neutral sodium and potassium pyrophosphates are much more effective than the corresponding orthophosphates. Since then, Heintze and Mann² have shown that various organic hydroxy-acids are almost as effective as pyrophosphate, and much more effective than the corresponding unsubstituted acids, as soil-manganese extractants.

From the start of this work it was obvious that there was a close parallel between the colour of an extract and its manganese content; pyrophosphate, malate, citrate, etc., gave dark extracts rich in manganese, while orthophosphate, succinate, tricarballylate, etc., gave light-coloured extracts poor in manganese. The original observations of Dion and Mann¹ and Heintze³ had already led Bremner and Lees (unpublished) to explore the possibility of using pyrophosphate as an extractant for soil organic matter (the nitrogen content of an extract was used as an index of its richness in organic matter), and, as these investigations showed that pyrophosphate was in fact a good organic-matter extractant, the new observations of Heintze and Mann prompted a similar investigation into the possibility of using malate, etc., for the same purpose. The results obtained showed that the hydroxy-acids were almost as effective as pyrophosphate, and the present joint