



Fig. 1. Chromatograms illustrating the effect of heating sugar solutions. (a) Hydrolysate from *Urena lobata*; (b) rhamnose fraction of the hydrolysate after boiling; (c) rhamnose fraction from the hydrolysate eluted with cold water; (d) pure rhamnose solution after boiling; (e) pure rhamnose; (f) pure xylose solution after boiling; (g) pure xylose

the rhamnose separated out from the main hydrolysate, was eluted with cold distilled water, and the resultant chromatogram (Fig. 1,c), obtained as usual, showed only the single spot corresponding to rhamnose. Thus it would appear that the rhamnose isolated from the fibre hydrolysate was uncontaminated by other sugars, and that epimerization or other structural change had occurred by and during the heating of the aqueous solution. It seemed scarcely feasible that alkaline conditions could have arisen either from the glassware, which was of well-used 'Pyrex', or from the filter-paper, in view of the acidity of the solvent used. Confirmation that structural transformation occurs on heating rhamnose in non-alkaline solution was obtained by refluxing a solution of chromatographically pure rhamnose (Fig. 1,d) in distilled water for 12 hr., during which period the pH of the solution fell to a value of 3.9 (Fig. 1,e).

The conversions occurring are not confined to the methyl pentose, since xylose solution, which yielded a single spot on a chromatogram (Fig. 1,g), showed additional spots after boiling for 12 hr. (Fig. 1,f).

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¹ Laidlaw, R. A., and Reid, S. G., *Nature*, **166**, 476 (1950).

² Duff, R. B., *Chem. and Indust.*, 898 (1953).

Effect of Chelating Agents on Heavy Metal Catalysis

In a recent communication, Pirie and Van Heyningen¹ have reported "a case where a chelating agent accelerated the oxidation of a substance (glutathione), which it was intended to preserve in the reduced state"¹. The object of the chelating agent was "the removal of metals", traces of which would presumably catalyse the oxidation. Since chelating agents are being generally used for this purpose, it seems worth while emphasizing that the metal chelate complexes formed are not necessarily without catalytic activity. Thus 1:10 phenanthroline, $\alpha\alpha'$ -di-pyridyl and $\alpha\alpha'\alpha''$ -tripyridyl increase the iron-catalysed rate of decomposition of hydrogen

peroxide by as much as one hundred-fold², and certain haemoprotein complexes of iron are well known as catalysts in biological systems.

We are studying the effect of chelating agents on the metal-catalysed autoxidation of cyclohexene. Only in the case of copper has the metal chelate complex been found to be catalytically inactive. In the case of iron, the formation of the chelate complex greatly increased the rate of the reaction. Approximate results are quoted in the table for the reaction at 60° C. in the presence and absence of 2 gm. mol. of NN'-disalicylidene ethylene diamine per gm. mol. of the metal heptoate.

Metal, initial valency state and concentration	Extent of oxidation after 60 min. reaction (gm. oxygen/kgm. cyclohexene)	
	No chelating agent	Disalicylidene ethylene diamine present
Cu ^{II} 50 p.p.m.	13	0.12
Fe ^{III} 500 p.p.m.	1.3	c. 60
Mn ^{II} 49.5 p.p.m.	21*	25
Co ^{II} 49.1 p.p.m.	27	36*
Metals absent	0.12	0.12

* Durations of these reactions are taken as 60 min. from the termination of the induction periods.

The formation of the chelate complex has little effect on the manganese-catalysed reaction. The kinetic characters of the two cobalt-catalysed reactions are completely different, however. In the absence of disalicylidene ethylene diamine the rate decreases, but in its presence the rate increases during the initial course of the reaction. The effect of a chelating agent sequestering copper but 'vivating' iron has also been established by us for the autoxidation of cyclohexene in the presence of NN'-dicyclohexyldithiooxamide. Further, we have observed a similar phenomenon for the autoxidation of sodium sulphite in aqueous solution, thus indicating that it is by no means confined to non-aqueous media.

The foregoing results show that not only metal ions but also covalently bound metals can be effective catalysts for free-radical chain-reactions. The fact that copper catalysis is prevented by chelation may result from the special condition that cuprous-cupric transitions probably involve large free energies of activation when the metal is chelated. Both cuprous and cupric copper have a normal co-ordination number of four, but the former requires a tetrahedral and the latter a planar disposition. Iron, however, will co-ordinate octahedrally in both valency states. Moreover, a quadridentate chelating agent may sterically prevent reaction in the case of a metal with a normal co-ordination number of four if the electron transfer mechanism requires the reacting molecule to enter the co-ordination shell of the metal. The study of hexadentate chelating agents for metals with a maximum co-ordination number of six should throw further light on these possibilities. Work is continuing in this direction.

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¹ Pirie, A., and Van Heyningen, R., *Nature*, **173**, 873 (1954).

² Baxendale, J. H., "Advances in Catalysis", **4**, 62 (1952).