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Preparation of Vitamin E Using Cation Exchange Resin Complexes of Metal Ions

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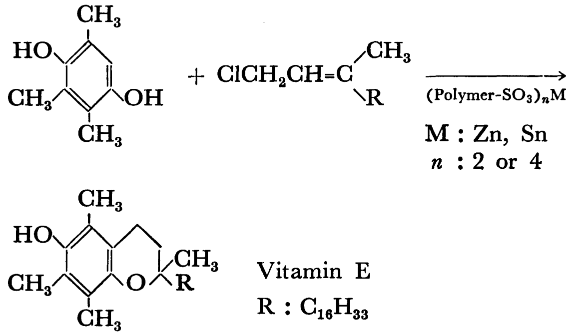
Synopsis. A series of cation exchange resin complexes of metal ions were prepared. These resins are effective catalysts for the preparation of vitamin E and were recycled for use several times with little activity loss. The effect of solvents and metal ions on the reaction is discussed.

Incresed attention has recently been paid to anchoring homogeneous transition metal catalysts to polymers. Heterogenized catalysts have some advantages over their homogeneous counterparts such as (1) the ease in separation from the product,[1–5] (2) enhanced size and positional selectivity,[6] and (3) the ability to carry out sequential catalytic reactions.[7] In this respect, insoluble polymers also have been used widely in organic synthesis,[8] for example, as protecting groups[9–11] or in esterification.[12–13]

The cation exchange resins were employed for the preparation of vitamin E, but their catalytic activity was very low. The present paper describes the preparation of cation exchange resin complexes of metal ions and the use of these materials as catalyst for the preparation of vitamin E.



It was shown that the catalysts can be used as heterogenous catalysts. Furthermore, the investigation of the preparation of vitamin E using the resin complexes as catalysts was prompted by the following advantages offered by resins: the ability to remove the catalyst from the reaction product by simple filtration, thus avoiding contamination of the latter and generating economic savings effected by repeated use of the resin, which exhibits good stability of activity. The stabilities of the catalysts decrease in the order $Sn^{4+} > Sn^{2+} > Zn^{2+}$. This agrees well with the stability order for chelate rings. In benzene, the catalysts were recycled several times with little loss in activity. However, in highly polar solvents such as acetonitrile, repeated use of the catalysts was not possible. This may be due to the elimination of metal ions from the resin by strong solvation. With recycling of the catalyst, a decrease in activity was observed. This is ascribed to the elimination of metal ions through reactions. The catalysts can be regenerated to their initial activity by the addition of the amount of metal ions equal to that lost in the reactions. The results are summarized in Table 1 and Fig. .

TABLE 1. EFFECT OF RECYCLING CATALYSTS
Trimethylhydroquinone: 50 mmol, phytyl chloride: 50 mmol, catalyst: 20 mmol (as metal ion), benzene: 50 ml and time: 3.0 h.

Metal ion	Run	Yield (%)	Purity (%)
Sn^{4+}	1	86.7	96.4
	2	86.0	94.1
	3	85.6	90.8
	4	82.5	89.5
	5	80.2	85.4
Sn^{2+}	1	87.4	94.9
	2	85.7	90.0
	3	84.7	88.5
	4	81.2	83.6
	5	75.4	80.1
Zn^{2+}	1	85.0	92.4
	2	83.5	90.6
	3	81.3	86.4
	4	75.6	80.4
	5	70.1	76.9

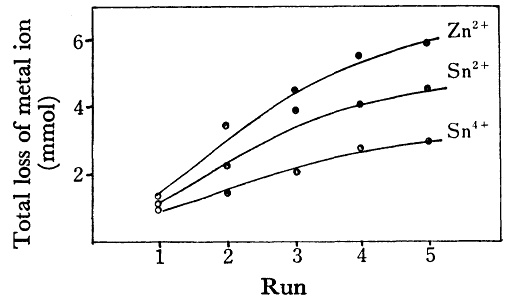


Fig. 1. Loss of metal ions.
Trimethylhydroquinone 50 mmol, phytyl chloride 50 mmol, catalyst 20 mmol (as metal ion), benzene 50 ml and time 3 h.

One practical limitation of this method is the very low catalytic activity and the inability to employ recycling when phytol or isophytol is used. In the course of the reaction, about 70% of the metal ions in the resin catalyst were detected. This strongly indicates that the catalytic species is a metal halide. These reactions were effectively assisted by the addition of a trace amount of a protonic acid, such as *p*-toluenesulfonic or methanesulfonic acid. This may be due to the promotion of cyclization in the reaction.[14] From the results, a plausible mechanism for this catalytic system is shown below. The detailed nature of the catalytic process reported here requires further clarification and work in progress is aimed at exploring the synthetic utility of this technique.

$$2\,\text{Polymer-SO}_3\text{H} + \text{ZnCl}_2 \longrightarrow (\text{Polymer-SO}_3)_2\text{Zn} + 2\text{HCl}$$

$$\begin{array}{l} 2\,\text{trimethylhydroquinone} + 2\,\text{phytyl chloride} \\ \xrightarrow[(\text{Polymer-SO}_3)_2\text{Zn}]{\hspace{3cm}} 2\,\text{Vitamin E} + \underline{\text{ZnCl}_2 + 2\,\text{Polymer-SO}_3\text{H}} \\ \hspace{7.5cm}\upharpoonleft\!\downharpoonright \\ \hspace{5.5cm}\underline{(\text{Polymer-SO}_3)_2\text{Zn} + 2\,\text{HCl}} \end{array}$$

or,

$$\begin{array}{l} \text{trimethylhydroquinone} + \text{phytyl chloride} + \text{ZnCl}_2 \\ \xrightarrow[\text{H}^+(\text{HCl or Polymer-SO}_3\text{H})]{\hspace{3cm}} \text{Vitamin E} + \text{ZnCl}_2 + \text{HCl} \end{array}$$

Experimental

GLC and atomic absorption spectra were recorded on a Hitachi 023 gas chromatograph equipped with a flame ionizer detector and a Hitachi 208 atomic absorption spectrometer, respectively.

General Procedure. Zinc chloride (12.3 g, 0.09 M) was dissolved in 100 ml of ethyl acetate. Amberlyst 15 in hydrogen ion form (30 g, 4.8 meq/g dry resin) was added to the solution and the mixture was maintained at 40 °C for 2 h and allowed to stand overnight at room temperature. The resin complex was filtered and washed well with acetone to remove hydrogen chloride and unbounded zinc chloride. A theoretical amount of zinc ions were shown to be bounded to the resin (analyzed by atomic absorption spectroscopy). A benzene solution (100 ml) containing 30 g of trimethylhydroquinone, 65 g of phytyl chloride and 30 g of the catalyst was allowed to reflux for 3 h. After standing overnight, the catalyst was filtered off and washed with acetone. The filtrate was concentrated under reduced pressure and the residue was subsequently distilled. The product thus obtained was analyzed by GLC. The catalyst could be recycled for use in the next reaction.

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References

1) C. P. Tsonis and M. F. Farona, *J. Organomet. Chem.*, **114**, 293 (1976).

2) K. G. Allum, R. D. Hancock, I. V. Howell, S. McKenzie, R. C. Pitkethly, and R. J. Robinson, *J. Organomet. Chem.*, **87**, 203 (1975).

3) K. G. Allum, R. D. Hancock, I. V. Howell, T. E. Lester, S. Mckenzie, R. C. Pitkethly, and P. J. Robinson, *J. Organomet. Chem.*, **107**, 393 (1976).

4) C. U. Pittman, Jr., L. R. Smith, and R. M. Hanes, *J. Am. Chem. Soc.*, **97**, 1742 (1975).

5) J. Basset, R. Mutin, G. Descotes, and D. Sinou, *C. R. Acad. Sci. Paris*, **280**, 1181 (1975).

6) C. U. Pittman, Jr., S. E. Jacobson, and H. Hiramoto, *J. Am. Chem. Soc.*, **97**, 4774 (1975).

7) C. U. Pittman, Jr., and L. R. Smith, *J. Am. Chem. Soc.*, **97**, 1749 (1975).

8) P. Hodge and G. Richardson, *J. Chem. Soc., Chem. Commun.*, **1975**, 622.

9) E. C. Blossey, L. M. Turner, and D. C. Neckers, *J. Org. Chem.*, **40**, 959 (1975).

10) J. M. J. Frechet and K. E. Haque, *Tetrahedron Lett.*, **35**, 3055 (1975).

11) J. M. J. Frechet and G. Pelle, *J. Chem. Soc., Chem. Commun.*, **1975**, 225.

12) G. D. Nageshwar, D. M. Pandharpurker, and P. S. Mene, *Chem. Age. India*, **26**, 365 (1975).

13) J. Yamanis and M. Adelman, *Can. J. Chem. Eng.*, **53**, 536 (1975).

14) P. A. Wehrli, R. I. Fryer, and W. Metlesics, *J. Org. Chem.*, **36**, 2910 (1971).