Heterogeneous Metathesis of Unsaturated Fatty Acid Esters

By Evert Verkuijlen,* Freek Kapteijn, Johannes C. Mol, and Cornelis Boelhouwer
(*Institute for Chemical Technology, University of Amsterdam, Plantage Muidergracht* 30, *Amsterdam, The Netherlands*)

Summary Rhenium heptoxide on alumina, promoted by a small amount of tetramethyltin, is an active and very selective catalyst for the heterogeneous metathesis of unsaturated fatty acid esters.

Whereas a few catalyst systems have been reported to be active for the homogeneous metathesis of unsaturated fatty acid esters,[1-3] so far the heterogeneous metathesis of these compounds has not been reported. We have found that with rhenium heptoxide on alumina (a well known catalyst for the heterogeneous metathesis of alkenes[4]) to which a small amount of Me_4Sn is added, the heterogeneous metathesis of these fatty acid esters can easily be performed.

The reactions were carried out in a stirred glass batch reactor at 323 K. The Re_2O_7–Al_2O_3 catalyst was prepared by impregnation of γ-Al_2O_3 with an aqueous solution of ammonium perrhenate, followed by drying at 383 K and calcining in dry air at 823 K. In a typical example methyl pent-4-enoate was metathesized into ethene and dimethyl oct-4-enedioate as follows. Re_2O_7–Al_2O_3 (1 g; 60—80 mesh, 22% Re_2O_7 by weight, surface area 240 $m^2 g^{-1}$) was activated in the usual way by heating at 823 K in a stream of dry air for 3 h, followed by heating in nitrogen for 1 h. After activation the catalyst was introduced into the reactor. CCl_4 (1 ml) was introduced through a septum, followed by Me_4Sn (5 μl; 0·036 mmol) and methyl pent-4-enoate (1 ml; 7·9 mmol). Samples were taken from the gas phase. G.l.c. analysis showed that ethene was formed immediately, in accordance with reaction (1). The presence of ethene in the gas phase was confirmed by i.r. spectroscopy. After 1 h the solid catalyst material was separated from the liquid phase by centrifugation. G.l.c. analysis of the liquid phase showed that only one new component was formed. The liquid components were separated by vacuum distillation. The newly formed product was identified as the expected diester by n.m.r. [δ 2·27 (CH_2), 3·60 (OMe), and 5·46 (=CH–)], i.r., and mass spectroscopy (*m/e* 200). The conversion of the monoester was 51%. The selectivity to the primary metathesis products was > 99%. The only by-product was a small amount of methane in the gas phase (due to the decomposition of the Me_4Sn).

$$2\ CH_2{=}CH[CH_2]_2CO_2Me \rightleftharpoons CH_2{=}CH_2 + MeO_2C[CH_2]_2CH{=}CH[CH_2]_2CO_2Me \quad (1)$$

Under the foregoing conditions the catalyst showed no activity for this reaction without activation or without the addition of Me_4Sn. In this respect it is noteworthy that Me_4Sn-containing catalyst systems exhibit optimum selectivity and activity for the homogeneous metathesis of unsaturated fatty esters.[1]

The catalyst system and the procedure have not yet been optimized. Preliminary experiments showed that with the above described system other unsaturated esters can also be metathesized.

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.). We thank F. van Elsäcker and G. C. N. van den Aardweg for technical assistance and AKZO Chemie Nederland for the Me_4Sn.

(*Received*, 14*th January* 1977; *Com.* 030.)

---

[1] P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, *J.C.S. Chem. Comm.*, 1972, 1221; *J. Amer. Oil Chem. Soc.*, 1974, **51**, 389.
[2] E. Verkuijlen and C. Boelhouwer, *J.C.S. Chem. Comm.*, 1974, 793.
[3] R. Nakamura, S. Fukuhara, S. Matsumoto, and K. Komatsu, *Chem. Letters*, 1976, 253.
[4] J. C. Mol and J. A. Moulijn, in 'Advances in Catalysis,' vol. 24, p. 131, Academic Press, New York, 1975.