Metathesis of Fatty Esters Derived from South African Sunflower Oil

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The metathesis of the mixture of fatty monoesters derived from sunflower oil was examined using the WCl_6-$(CH_3)_4Sn$ catalytic system. After distillation of the reactant mixture, a total conversion of 81% and a 17% yield of diesters was achieved using a 1:1:30 mole ratio of catalyst:cocatalyst:ester. The rate of reaction of the ethyl linoleate was double that of the oleate.

The metathesis of fatty esters using the WCl_6-$(CH_3)_4Sn$ catalytic system was first described in 1972 (1). Since then numerous publications have appeared dealing with the metathesis of esters such as methyl oleate (2), methyl linoleate (3), methyl linolenate (4) and others (5), as well as the metathesis of fatty oils (6). The heterogenous catalysts Re/Al_2O_3 (7) and Re/SiO_2-Al_2O_3 (8) have also been successfully employed for the metathesis of these unsaturated esters. Of interest to us was the synthesis of the diesters (for polymerization purposes) via the metathesis of the mixture of monoesters as obtained from the vegetable oils. Whereas previous reports have dealt with single-component fatty ester systems (9-11), in this communication we report on the tungsten-catalyzed metathesis reaction of the mixture of unsaturated acid esters that were derived from South African sunflower oil.

MATERIALS AND METHODS

The major constituents of the ester mixture were 6% ethyl stearate, 7% palmitate, 28% oleate and 59% linoleate. The ester mixture was distilled (12) and then degassed with nitrogen prior to use. The catalytic experiments were carried out in a two-necked flask which was fitted with a rubber septum and a condenser, on top of which a T-piece was placed to allow for a continuous flow of nitrogen.

WCl_6 (99.9+% pure) and $(CH_3)_4Sn$ were purchased from Aldrich Chemical Co. (Milwaukee, WI). The addition of reagents was as previously described (13). Care was taken throughout all the steps to exclude air and moisture. In a typical experiment, 1.4 g of WCl_6, 40 ml of esters and 0.6 ml of $(CH_3)_4Sn$ were used. The reaction was carried out at 110-120°C. At the end of the reaction, the metal species was precipitated by adding an aqueous ammonia solution (2). Analyses were carried out by gas chromatography using FID with a BP-1 capillary column and an OV-101 packed column. The reaction mixtures were further analyzed by gas chromatography-mass spectrometry.

RESULTS AND DISCUSSION

After distillation and using a 1:1:30 mole ratio of catalyst:cocatalyst:ester, a total conversion of 81% of the linoleic and oleic esters was obtained. This compares favorably with the literature results of 84% conversion for the metathesis of pure methyl linoleate (4), and of 50-54% of methyl oleate (13), where a 1:1:50 mole ratio was used. Considerably lower conversions were obtained with the undistilled ester mixture.

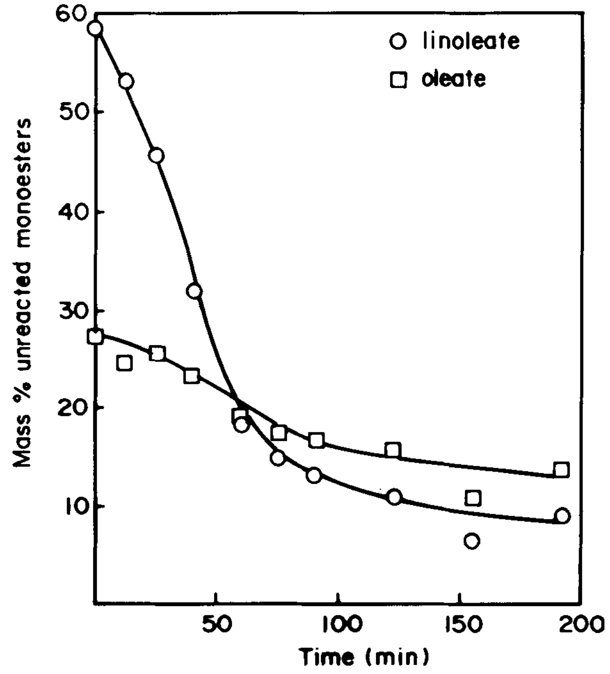

FIG. 1. Reactivity of the monoesters.

The reactivity of each of the unsaturated esters present in the reactant mixture was monitored with time and the results are shown in Figure 1. Within an hour, 69% of the linoleic and 33% of the oleic esters had reacted. After three hours, the conversions were 84 and 50%, respectively. The higher conversion rate of the linoleic esters compared to that of the oleic (ca. 2:1) could be attributed to the presence of two double bonds in the former, as compared to only one in the latter.

The reaction products (viz., alkenes, mono- and diesters) arising from the metathesis reaction of (i) a linoleic and linoleic ester, (ii) oleic and oleic, and (iii) linoleic and oleic, were identified by mass spectrometry. The products of the first two combinations are as previously reported in the literature (3,14). The only new products, a consequence of the third combination, were the C_6=C_9 and C_6=C_3=C_9 alkenes at m/e=210 and 250, respectively. Two diesters were observed, $EtOOCC_8$=C_8OOEt (m/e=368) and $EtOOCC_8$=C_3=C_8OOEt (m/e=408) (Et=ethyl), and the percent yield with time is shown in Figure 2. However, we have been unable to detect the $EtOOCC_8$=C_3=C_8COOEt diester or any others of higher molecular weight in the product mixture obtained under our reaction conditions. This species was previously observed (2.3 mol%) in the products arising from the metathesis of the pure linoleic ester (3). The influence, therefore, of the differences in the reaction conditions and of the use of a mixture of

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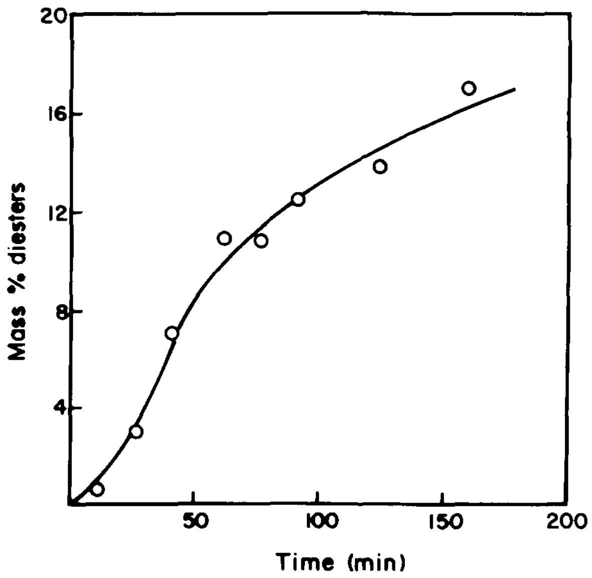

FIG. 2. Plot of percentage yield of diesters vs time.

esters resulting in secondary metathesis (of the highly unsaturated esters to produce lower molecular weight products) and a lower probability of formation, respectively, cannot be excluded. Thus, the metathesis of the mixture of unsaturated fatty esters derived from sunflower oil has been demonstrated. Under these reaction conditions, high conversions were obtained after a simple distillation of the reactant mixture.

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