Kinetics of Decomposition of Methyl Linoleate and Vapor-Liquid Equilibria in Mixtures of Methyl Palmitate and Methyl Linoleate

Stephen R. Goodwin[1] **and David M. T. Newsham**[2]
Department of Chemical Engineering, University of Manchester Institute of Science and Technology,
Manchester M60, 1QD, England

The rates of thermal decomposition of methyl linoleate are measured in the liquid phase over the temperature range 265–320°C. The kinetics are first order with respect to methyl linoleate, and the rate constants can be represented by the expression k (min) = 6.5 × 10^9 exp [−(16700 ± 5000) K/T]. Vapor-liquid equilibria of mixtures of methyl linoleate and methyl palmitate are also determined at 30 mm Hg together with the vapor pressures of the pure components.

One technique for the separation of fatty acids is to first form the methyl esters which can then be separated by distillation with relative ease. The thermal instability of the methyl esters of fatty acids usually requires use of vacuum distillation, and for reliable design both kinetic data on decomposition rates and phase equilibria are required. This paper reports such data for the system methyl linoleate and methyl palmitate.

Experimental

Materials. The methyl palmitate (Kodak Chemicals, technical grade) was purified by vacuum fractionation, and gas chromatographic analysis showed no significant impurities. The refractive index of the sample was 1.4334 at 40°C compared to a value of 1.4317 at 45°C determined by Monick et al. (*4*).

The sample of methyl linoleate (Koch Light Chemicals) contained 1 wt % of methyl stearate and 14 wt % of methyl oleate after fractionation to remove other impurities. The stearate, oleate, and linoleate have the same number of carbon atoms and are structurally identical except for the degree of saturation; the stearate alkyl chain is fully saturated, the oleate has one double bond and the linoleate two. Their boiling points at 10 mm Hg are 207.3°, 205.3°, and 206.1°C, respectively, and they cannot be separated by ordinary distillation. No attempt was made to remove the oleate and stearate.

Analysis. The compositions of the esters were determined using a Perkin-Elmer Model 900 gas chromatograph and a 2-m column packed with diethylene-glycol succinate on Chromosorb W HMDS. The column temperature was maintained at 180°C. Thermal decomposition of the linoleate on the column was discouraged by use of the deactivated solid support and by operating with a high carrier gas flow rate (helium at 60 ml/min).

Decomposition kinetics. The rates of decomposition of methyl linoleate were investigated by following the change in linoleate concentration by gas-liquid chromatography. Thoroughly degassed samples were sealed under vacuum in glass reaction tubes and maintained at a fixed temperature (±0.1°C) in an air thermostat. This procedure was carried out at three temperatures between 265° and 320°C. A set of experiments was also carried out at 300°C with samples which had not been degassed, to investigate the effect of air on the rate of decomposition. The first order rate constants for each temperature were obtained from the slopes of plots of ln c_0/c against time. The rate constants were then fitted to the usual Arrhenius expression (Figure 1) from which we find k (min) = 6.5 × 10^9 exp [(−16700 ± 5000) K/T] and an activation energy of (33 ± 10) kcal mol^{-1}.

Phase equilibria. The equilibrium flow still used for the measurements of vapor-liquid equilibria has been described previously (*2*). Its main feature is a low residence time which allows measurements to be made without significant thermal decomposition of the samples. Although the commercial methyl linoleate sample contained significant amounts of impurities, the properties of the latter are so similar to those of pure methyl linoleate that for the purposes of this investigation, the mixtures of methyl palmitate and commercial methyl linoleate have been considered pseudobinary.

The boiling points of the esters at different pressures are given in Table I. The equilibrium vapor and liquid compositions at 30 mm Hg for the pseudobinary mixtures are recorded in Table II and Figure 2. The mole fractions quoted for methyl palmitate are true mole fractions, whereas those for methyl linoleate refer to a mixture of linoleate, oleate, and stearate in the ratio *85:14:1* by weight. The root-mean-square deviation of the vapor compositions from the smooth curve of Figure 2 is 0.5 mol %.

Discussion

The thermal decomposition of methyl linoleate has been studied by several workers. In the absence of air, a mixture of dimers is produced (*5*), while decomposition in the presence

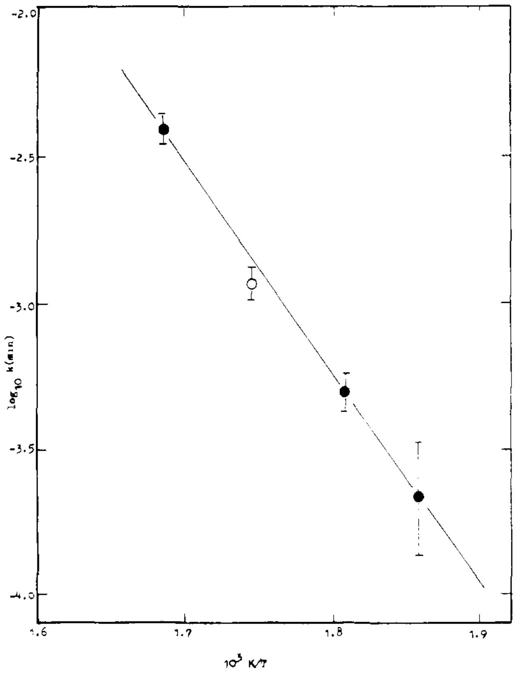

Figure 1. Rate constants for decomposition of methyl linoleate. ●, Air-free samples; O, aerated sample

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[1] Present address, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto 5, Ont., Canada.
[2] To whom correspondence should be addressed.

Table I. Boiling-Point Temperatures for Methyl Palmitate and Methyl Linoleate

Methyl palmitate		Methyl linoleate	
P, mm Hg	*t*, °C	*P*, mm Hg	*t*, °C
14.7	190.9	14.5	213.2
18.6	198.3	19.8	219.6
22.3	205.3	25.2	225.4
30.3	210.5	29.7	230.4
38.9	217.9		
48.3	224.3		

Table II. Vapor-Liquid Equilibrium Data for Methyl Palmitate(1)-Methyl Linoleate(2) at 30 mm Hg

x_1	y_1	*t*, °C
0.042	0.088	229.3
0.205	0.357	225.4
0.310	0.486	222.3
0.407	0.584	221.2
0.587	0.743	216.6
0.630	0.781	216.6
0.742	0.861	214.8
0.833	0.912	213.1
0.925	0.965	212.0

of air produces many polymeric compounds, including aromatics (*3*). Sterk (*6*) found a value of 11.2 kcal/mol for the activation energy of the polymerization of methyl linoleate in a nitrogen atmosphere, using nmr spectroscopy. This does not agree at all well with our value of (33 ± 10) kcal/mol. The decomposition reaction has also been investigated under vacuum by Figge (*1*) who reports $k = 0.031$ hr^{-1} at 280°C which agrees very well with our value of $k = 0.030$ hr^{-1} at the same temperature. Figure 1 shows that the rate constant determined in the presence of air does not differ significantly from that expected in an air-free experiment, despite the different reaction products.

Nomenclature

k = rate constant, min^{-1}
t = Celsius temperature, °C

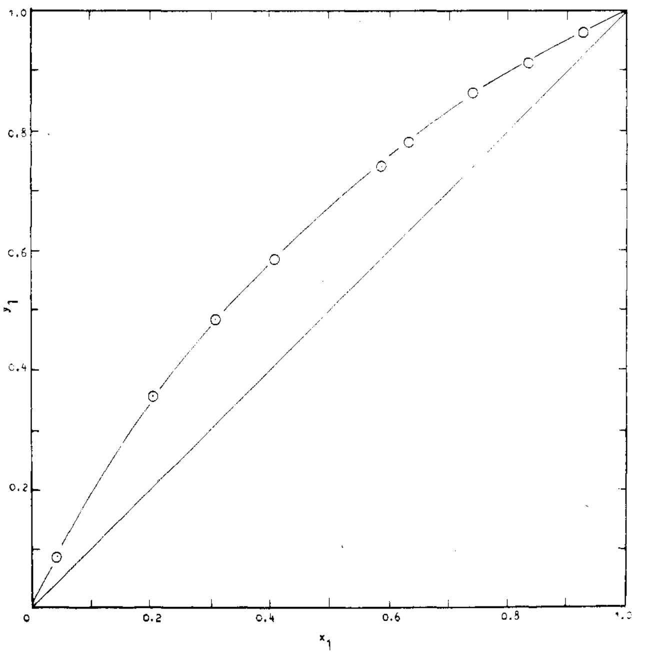

Figure 2. Equilibrium vapor and liquid compositions for methyl palmitate(1)-methyl linoleate(2) at 30 mm Hg

T = Kelvin temperature, K
c = concentration, wt %
c_0 = initial concentration, wt %
y_1 = vapor-phase mole fraction
x_1 = liquid-phase mole fraction

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