Thermal Analysis of 1,2-Epoxypropyl Esters of Normal Fatty Acids

ABSTRACT

Seven members of this homologous series have been studied by differential scanning calorimetry (DSC), and their melting point, enthalpy and entropy of fusion obtained. The entropy change for each additional carbon-carbon bond in the aliphatic acid chain closely observed the value *R ln* 3, as expected for flexible molecules. IR spectra of crystalline glycidyl miristate, palmitate and stearate showed the typical band progression in the 1180-1350 cm^{-1} region and a doublet at ca. 720 ± 10 cm^{-1}. Glycidyl esters appeared to be free of polymorphism, since no differences in the behavior of solids crystallized from solvent or from the melt were observed either by DSC or by IR spectroscopy.

INTRODUCTION

The entropy of fusion of *n*-alkanes increases by a factor of ca. *R ln* 3 per each additional methylene group in the hydrocarbon chain, as was noted by Aranov et al. (1) and attributed to the fact that, at the onset of melting, the molecules become free to undergo rotations through the three most probable minima about each carbon to carbon bond. Several homologous series of paraffin derivatives have been checked for that behavior (2), including complex lipids of biological interest exhibiting mesophase transitions (3,4). The major aim of the present work was the study of the calorimetric behavior of several glycidyl esters.

EXPERIMENTAL PROCEDURES

The esters were prepared from the sodium salt of the fatty acid according to the method of Maerker et al. (5). Thin layer and gas liquid chromatography, chemical analysis, mass spectrometry and NMR spectroscopy (Olano and Martín-Lomas, unpublished) and IR spectroscopy demonstrated that the purity of the products was always higher than 99.8%; calorimetric analyses of some members of the series were consistent with that figure.

Melting temperatures were determined by means of a differential scanning calorimeter Perkin-Elmer DSC-1B whose temperature response was calibrated with the melting points of *n*-undecane, *n*-tetradecane, *n*-nonadecane, *n*-hexatriacontane and stearic acid, all over 99.9% pure. Heats of fusion were measured from the endothermic peaks after area-to-calories conversion by both planimeter measurements and weighing of the fusion area of indium (semiconductor grade). The analysis of each particular ester involved six samples of different weights ranging between 1 and 4 mg (±0.02), and every sample was scanned three times. The first thermogram was always rejected to eliminate curve perturbations, and the remaining pair was used to determine both melting temperatures and heats of fusion. In the case of area evaluations, one thermogram of each couple was measured with a planimeter and the other was cut out and weighed.

IR spectra were recorded at room temperature on a Perkin-Elmer Model 457 apparatus by using the potassium bromide technique (1 mg ester per 300 mg KBr).

RESULTS AND DISCUSSION

Seven members of glycidyl esters of even *n*-fatty acids from hexanoate to octadecanoate were studied. Phase transitions were not observed upon repetition of the analysis on samples recrystallized from the melt under different thermal treatments. The results are shown in Table I.

According to statistical analysis, melting temperatures were reproducible within 0.08% and heat of fusion within 2%. Heat and entropy of fusion data show linear relationships with hydrocarbon chain lengths (0.99 of correlation coefficients), their slopes being 1.04 Kcal/mol per C-C bond and 2.70 cal/mol K per C-C bond, respectively. These values, representing the configurational contributions for each additional methylene group in the *n*-alkane chain to the enthalpy and entropy of fusion of the series, agree satisfactorily with the theoretical values of *R*/2 and *R ln* 3, respectively.

IR spectra of the three higher members of the series in the crystalline state showed the typical band progression in the 1250 cm^{-1} region, corresponding to the twisting and wagging vibrations of the methylene groups in long chain substances, as recorded in Table II, where the frequency accuracy is ca. ±2 cm^{-1}.

Similarly to glycerides of even saturated fatty acids, this zone was characterized by uniformity in the spacing and number of bands, this being half the number of carbon atoms in the acyl chain (6). On the other hand, the three

TABLE I

Calorimetric Data of Glycidyl Esters

Acyl chain	Melting temperature, K	Enthalpy of fusion, kcal/mol	Entropy of fusion, cal/mol K
n-Hexanoate	242.2	5.36	22.2
n-Octanoate	260.5	6.97	26.8
n-Decanate	281.8	9.15	32.5
n-Dodecanate	296.4	11.67	39.4
n-Tetradecanate	307.5	13.30	43.3
n-Hexadecanate	317.1	15.37	48.5
n-Octadecanate	325.0	17.72	54.5

TABLE II

Band Progression in 1180-1350 cm^{-1} Region of IR Spectra of Glycidyl Esters in Solid State

Ester	Frequency of bands, cm^{-1}								
Miristate	1351	1328	1306	1280	1255	1228	1201		
Palmitate	1350	1328	1310	1288	1265	1242	1219	1197	
Stearate	1347	1328	1312	1292	1273	1254	1233	1213	1193

spectra showed a doublet at ca. 718 and 729 cm^{-1}, suggesting some kind of perpendicular arrangement among the hydrocarbon chain planes, as in β' forms glycerides.

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Electron Spin Resonance of Free Radicals Formed in Irradiated Fatty Acid Methyl Esters

ABSTRACT

A composite nonsymmetrical electron spin resonance signal was detected in unsaturated fatty acid methyl esters (FAME) irradiated in quartz by a γ-ray dose of 500 Krad at liquid nitrogen temperature. The signal spread over a width of ca. 20 G with a spectroscopic splitting factor value of ca. 2.038, but contained an interference from the irradiated quartz. A narrower signal($\simeq$6 G) with a spectroscopic splitting factor value of 2.0361 was detected in the unsaturated FAME irradiated by UV, and was devoid of the hyperfine structure. No signal could be detected in methyl stearate irradiated by UV under the same conditions.

The autooxidation of unsaturated fatty acids is almost universally accepted to occur via a free radical mechanism in which electromagnetic energy, among other factors, plays an important role in the initiation step (1). Since electron spin resonance spectroscopy (ESR) responds only to the presence of unpaired electrons, it provides the best direct approach for ascertaining the presence of free radicals. Free radicals have been detected by ESR during ozonization of linoleic acid (2) and in the reaction of nitrogen dioxide with unsaturated fatty acids and phospholipids (3). However free radicals could not be detected by ESR, under the most favorable conditions, during the peroxidation of arachidonate in aqueous emulsions (4). On the other hand, it was demonstrated that fish protein concentrates with added highly unsaturated fatty acids exhibited a characteristic ESR signal when lipid oxidation occurred (5).

ESR has been applied to the study of the free radicals formed in triglycerides upon high energy irradiation. The types of radicals produced were found to vary with both the substrate and temperature of irradiation (6,7). The free radicals formed in several fatty acids upon irradiation have also been investigated (8,9). No radicals could be detected by ESR in fatty acids oxidized by air, irradiated by UV, or by a γ-ray dose of less than 1.0-1.2 Mrad. This communication reports an attempt to detect and study the free radicals formed by γ or UV irradiation of some unsaturated fatty acid methyl esters (FAME).

About 200 mg of the high purity FAME, Hormel Institute, was placed in a thin-walled 4 mm OD Spectrosil quartz tube and degassed by alternative freezing and warming five times under high vacuum (5-10 μ). The tubes were sealed and then irradiated in a Dewar flask filled with liquid nitrogen (-196 C). The γ source was a C0^{60} Gamma Cell 220 designed by Atomic Energy of Canada Ltd., and the dose applied was measured by a Fricke-Miller dosimeter. In the case of UV irradiation, the Dewar flask was made of quartz and the light source was a 500 W mercury arc lamp, PEK, Model 915 L.H., Sonnyvale, Calif. The light was passed through a 5 cm wide water filter to eliminate IR light and then focused on the sample placed ca. 15 cm from the lamp. Condensation of moisture on the outer wall of the Dewar flask was prevented by passing a jet of dried air around the flask. At the end of irradiation, the sample tube was transferred quickly to the spectrometer cavity, which was precooled to -196 C in order to prevent recombination of the free radicals. The spectra were recorded by using a Varian (V-4500-10A) X-band spectrometer utilizing 100 Kc/sec modulation. The spectrometer was fitted with a Fieldial (V-FR 2503) magnetic field regulator and an Alpha (M 3093) Digital NMR Gaussmeter.

The ESR spectra of the methyl esters of oleate, linoleate and linolenate irradiated at a dose of 0.5 Mrad revealed a nonsymmetrical signal that was almost identical for the three FAME examined. The composite signal spread over ca. 20 G and had a spectroscopic splitting factor (g) value of 2.038. A hyperfine structure was apparent but variant at higher irradiation doses. A smaller and similar signal was always present in the spectra of irradiated empty quartz tubes used as blanks. This is in disagreement with the re-