Total and Partial Erucate of Pentaerythritol. Infrared Spectroscopy Study of Relationship Between Structure, Reactivity, and Thermal Properties

Valérie Eychenne, Zéphirin Mouloungui*, and Antoine Gaset
Ecole Nationale Supérieure de Chimie de Toulouse, Laboratoire
de Chimie Agro-industrielle, Unité associé INRA n° 31A1010, Toulouse, France

ABSTRACT: Esters of neopentylpolyols are an important starting base for synthetic lubricants. These bulky esters are generally prepared by an esterification reaction between a carboxylic acid and a neopentylpolyol. Because neopentylpolyols have a number of primary alcohol sites, a variety of partial esters is formed before total esters. In the present study, we investigated the reaction between pentaerythritol and erucic acid. The composition of the reaction mixture in erucic acid, partial esters, and total esters was monitored by thin-layer chromatography, coupled with flame-ionization detection. The pure esters and the esters in solution at different concentrations in xylene at different temperatures were analyzed by Fourier transform infrared spectroscopy. Erucic acid and partial esters in xylene coexist in the free form and as bound complexes. These findings furthered understanding of the reactivity and thermal properties of the partial esters.

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KEY WORDS: Erucic acid, FTIR, partial esters, pentaerythritol, TLC–FID.

The exploitation of erucic acid forms part of a European development project (1). Erucic acid, a molecule with 22 carbons and a double bond at position 13, is found in crambe oil and high-erucic rapeseed oil. A large number of studies have been devoted to these plants in both the United States and Europe (2,3). The erucic oils have many advantages compared to oils with short chains (4,5) including fluidity, high viscosity, good stability at high temperature, and especially high flash and smoke points. These properties suggest applications in the field of lubrication.

Oils that consist mainly of triglycerides have a number of drawbacks. The presence of polyunsaturated molecules makes them sensitive to oxidation, and thermal *cis*-elimination (6) may occur owing to the presence of a β-hydrogen to the hydroxyl group.

By chemical modification, we have prepared a number of temperature-resistant structures. Because neopentylpolyols do not possess a β-hydrogen, only radical decomposition can occur, which requires more energy, giving rise to higher decomposition temperatures (6).

The flash point is the lowest temperature at which the application of a test flame causes the vapor to ignite. The flash point of the synthetic ester (erucate of pentaerythritol: >300°C) is higher than that of natural triglycerides (rapeseed oil: 280°C; crambe oil: 260°C). Pentaerythritol thus became the subject of our investigations.

In addition to good thermal and oxidative stability, neopentylpolyol esters have many other advantages (6), such as good viscosity/temperature behavior, low pour point, low volatility, good lubricity, and biodegradability. Neopentylpolyols esters would thus appear to be products of choice for lubricant or lubricant additives.

The present study was designed to examine relationships between structure, reactivity, and thermal properties. The total and partial esters of erucate of pentaerythritol were subjected to analysis by Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL PROCEDURES

Materials. Pentaerythritol [$C(CH_2OH)_4$, 98%] was supplied by Acros (Noisy le Grand, France). Erucic acid (C22:1, >95% pure) was purchased from Sigma (St. Quentin Fallavier, France). 4-Toluene-sulfonic acid (*p*-TSA, >99% pure) was obtained from Fluka (L'Isles d'Abeau Chesnes, France). Xylene, as a mixture of three isomers, was obtained from SDS (Peypin, France). 4-Xylene for IR analysis was of analytical grade (Fluka).

Esterification. Pentaerythritol (25 mmol), 110 mmol erucic acid, 2% *p*-TSA (based on alcohol weight), and 40 mL xylene were placed in a 200-mL flask and heated to 200°C. The flask was equipped with a mechanical stirrer, a thermometer, a Dean-Stark trap with a coolant, and a nitrogen input (inert atmosphere). To obtain the partial esters, the reaction could be stopped at any time.

Reaction monitoring. The reaction (Scheme 1) was followed by the thin-layer chromatography–flame ionization detection (TLC–FID) system (7) (Iatroscan, Iatron, Japan; French distributor: Bionis, Richebourg, France). One milliliter of solu-

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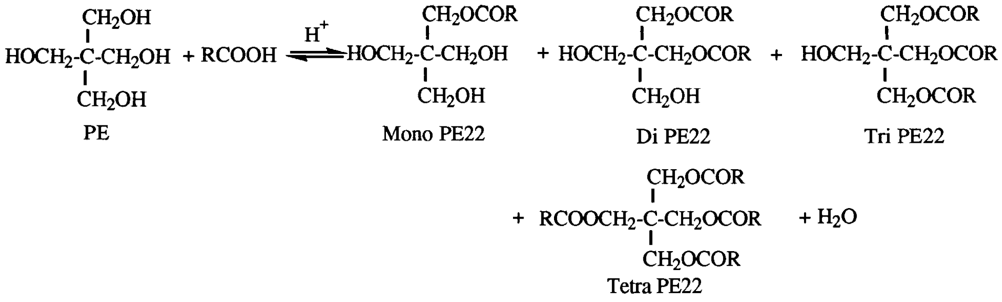
*To whom correspondence should be addressed at Ecole Nationale Supérieure de Chimie de Toulouse, Laboratoire de Chimie Agro-industrielle, 118, route de Narbonne, 31077 Toulouse Cedex, France.
E-mail: lcacatar@cict.fr.



SCHEME 1

tion [diluted in high-performance liquid chromatography (HPLC)-grade chloroform] was spotted onto S-III chromarods with an autospotter (model 3200/IS-01). The S-III chromarods are reusable quartz rods that are coated with silica gel particles of uniform shape and size. After spotting, the chromarods were placed for 20 min in 100 mL of eluant [hexane/diethyl ether/formic acid (80:20:0.04, vol/vol/vol) of HPLC grade]. The rods were dried in an oven at 120°C for 5 min and put for 5 min in a vacuum dessicator to reach room temperature. The scans were carried out on an Iatroscan MK 5 analyzer, connected to a 386 SX computer, which was used with Boreal Software (JMBS Developments, Fontanil Cornillon, France) for acquisition and analysis. The hydrogen and air flow rates of the FID were 160 and 1800 mL/min, respectively. The scanning speed was set at 3, which corresponded to 35 s/rod. A solution of 1 mg/mL of cholesterol was used as internal standard.

Purification. At the end of the reaction, all xylene was evaporated. After cooling, the residual oil was deacidified by an anionic resin to remove the catalyst and the excess of acid. The different esters were fractionated on a silica gel column with hexane that contained an increasing amount of diethyl ether. The purity of the products was determined by TLC with pentane/diethyl ether/formic acid (80:20:5, vol/vol/vol) as eluant. The spots were revealed with 2,7-dichlorofluorescein.

Characterization. The studies at different dilution and temperatures were carried out in a Perkin-Elmer model 1760X FTIR spectrometer. For the temperature studies, a T.V. SPECAC module was fitted to the IR spectrometer. The thermal analyses were carried out in a Setaram TG-DTA 92 apparatus (Calaire, France).

RESULTS AND DISCUSSION

Reaction monitoring. The reaction between pentaerythritol and erucic acid was speeded up by the acid catalyst, and the equilibrium was shifted by azeotropic elimination of the water formed and by use of excess acid at the start of the reaction. After two steps of purification, the tetraester (the total ester) and the mono-, di-, and triesters were obtained.

These molecules of high molecular weight and low volatility could not be readily analyzed by gas–liquid chromatography, and their wide range of polarity and their insolubility in many solvents ruled out HPLC. Exclusion chromatography did not give an effective separation because the mass difference between two peaks corresponded to only one molecule of acid: 338 g/mol. However, good separation was obtained by TLC. To quantitate the mixtures of compounds, we used the TLC–FID system, which combines the separation by TLC and FID. It represents a simple and rapid method for studying the progress of the reaction.

In 1981, Poré *et al.* (8) reported a kinetic study of the reaction between pentaerythritol and various fatty acids by TLC–FID. These analyses used rods coated with aluminum oxide (chromarod A) and required four successive developments in different solvent mixtures. We used a simpler method that required a single development. Errors from variation of the response of the rods were reduced by using an internal standard. A chromatogram obtained under our conditions is illustrated in Figure 1.

Pure products for the calibration were separated on a silica gel column. Structure and purity were confirmed by ^{1}H nuclear magnetic resonance (NMR) (Table 1) and ^{13}C NMR (Table 2) (9,10). The FID response is nonlinear (7,11), and the power curves are best fitted by the relationship $y = ax^b$. In Table 3, we list the relationships obtained with all pentaerythritol esters and erucic acid. Table 3 shows that the correlations (R^2) were good. In this way, we could follow the behavior of each component of the lipophilic medium (Fig. 2). The acid disappeared as the tetraester formed. The different partial esters appeared and disappeared at different rates. After 10 h of reaction, the mixture was composed of 70% tetraester,

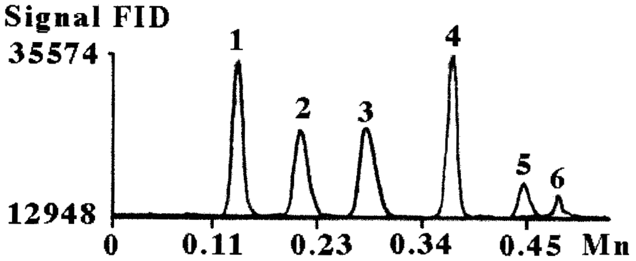


FIG. 1. Thin-layer chromatography–flame-ionization detection (TLC–FID) chromatogram (eluant: hexane/diethyl ether/formic acid, 80:20:0.04, vol/vol/vol; migration delay = 20 min, internal standard: cholesterol, 1 mg/mL). Peak 1, 0.14 tetra PE (pentaerythritol) C22:1; Peak 2, 0.21 acid C22:1; Peak 3, 0.28 tri PE C22:1; Peak 4, internal standard; Peak 5, 0.47 di PE C22:1; Peak 6, 0.50 mono PE C22:1.

TABLE 1
Nuclear Magnetic Resonance (NMR) ^1H, Chemical Shift (in ppm) of Esters of Pentaerythritol (PE) and Erucic Acid (30% in $CDCl_3$, vol/vol)[a]

	Multiplicity	Tetra PE22	Tri PE22	DI PE22	Mono PE22
H - C = C	*t*	5.33	5.33	5.33	4.54
CH_2 (B)	*s*	4.1	4.1	4.1	4.2
CH_2 (B′)	*s*	—	3.48	3.55	3.63
OH	*s*	—	2.61	NI	2.6
CH_2 (2)	*t*	2.28	2.31	2.33	2.33
CH_2 (α to C=C)	*d*	1.98	2.00	2.01	2.00
CH_2 (3)	*m*	1.59	1.60	1.56	1.58
Others CH_2	*m*	1.25	1.26	1.25	1.26
CH_3 (22)	*t*	0.87	0.87	0.88	0.87

[a] NI, Not identified.

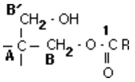
20% acid, 10% triester, 0% diester, and 0% monoester. The triester was still present in a nonnegligible proportion, although the mono- and diesters disappeared more rapidly. The shift of the equilibrium from the triester to the tetraester was slower than that for the other partial esters.

Structure–reactivity study. The OH band of erucic acid and the partial esters was monitored by FTIR, which provided information on their structures and reactive forms. Erucic acid, diluted in xylene at 0.01 M, exhibited two peaks in the OH stretching vibration range (Fig. 3). The first band at 3591 cm^{-1} was attributed to a free hydroxyl, and the second at 3443 cm^{-1} to a dimer form of the acid. Even at high dilution, the acid is mainly in a dimer form (12). The acid was thus assumed to react in the form of a dimer which is in line with the study of Bacaloglu *et. al.* (13) who proposed that fatty acids react with trimethylolpropane (another neopentylpolyol) in a dimer form *via* a cyclic intermediate that involves one molecule of alcohol, a monomer acid, and a dimer acid.

TABLE 2
NMR ^{13}C, Chemical Shift (in ppm) of Esters of PE[a] and Erucic Acid (30% in $CDCl_3$ vol/vol)[b]

	Tetra PE22	Tri PE22	Di PE22	Mono PE22
A	41.87	43.96	44.89	45.95
B	62.17	B) 62.02	B) 62.39	B) 62.69
		B′) 60.76	B′) 62.49	B′) 63.60
1	173.21	173.89	174.59	NO
2	34.21	34.21	34.26	34.32
3	24.91	24.97	25.00	25.05
12	27.25	27.27	27.25	27.26
13	129.89	129.94	129.95	129.92
14	129.89	129.94	129.95	129.92
15	27.25	27.27	27.25	27.26
20	31.95	31.96	31.95	31.96
21	22.73	22.74	22.73	22.73
22	14.14	14.17	14.16	14.17
Other CH_2	29–30	29–30	29–30	29–30

[a] Pentaerythritol esters:



$$-\overset{\overset{\displaystyle CH_2-OH}{|}}{\underset{|}{C}}-CH_2-O-\underset{\underset{\displaystyle O}{\|}}{C}R$$

[b] NO, not observed; see Table 1 for other abbreviation.

The partial esters also exhibited shifts in the OH stretching band. A single broad peak was observed with the pure partial esters (Fig. 4). According to Sakurai *et al.* (14), the peaks at 3425 and 3407 cm^{-1} for the mono- and diesters, respectively, were evidence for intermolecular association, while the peak at 3508 cm^{-1} for the triester corresponded to an intramolecular association.

Dilution in xylene modified the structures. We noted the appearance of two peaks (Fig. 5). Because xylene is a neutral and nondissociating solvent, dilution would not be expected to modify intramolecular hydrogen bonds. We observed the free hydroxyl stretching vibration in the 3600 cm^{-1} range. The bound form has a lower stretching vibration. Intermolecular bonds, modified by dilution, were observed toward 3400 cm^{-1}, while intramolecular bonds, not modified, were in the neighborhood of 3510 cm^{-1} (Fig. 6). The second band in Fig. 5 was therefore attributed to the intramolecular form. We also noted that the second peak was stronger for the triester, even in a highly dilute solution (0.005 M).The triester exists mainly in the “a” form (Fig. 6). The hydroxyl of the triester is less free, and consequently, less reactive than the hydroxyls of the mono- and diesters. This accounts for the slower disappearance of the triester. Even after 10 h of reaction, considerable amounts were still present in the mixture. The structure–reactivity relationship can be summarized as follows: (i) the acid reacts in the dimer form (13); (ii) mono and diesters exist mainly under the intermolecularly bound forms, bonds that are disrupted by dilution; and (iii) the triester has mainly intramolecular hydrogen bonds and is less reactive.

Structure–properties study. We measured the thermal stability of all separated esters (total and partial). This property is

TABLE 3
Calibration Curve Equations (relationship between the peak area and weight ratios)

Compounds[a]	Equations of type $y = ax^b$	Correlation coefficient
Tetra PE22	$y = 0.5773x^{1.5094}$	$R^2 = 0.9956$
Acid C22:1	$y = 0.4698x^{1.4821}$	$R^2 = 0.9933$
Tri PE22	$y = 0.4618x^{1.4216}$	$R^2 = 0.9985$
Di PE22	$y = 0.9517x^{0.981}$	$R^2 = 0.9982$
Mono PE22	$y = 1.8863x^{1.0313}$	$R^2 = 0.9934$

[a] See Table 1 for abbreviation.

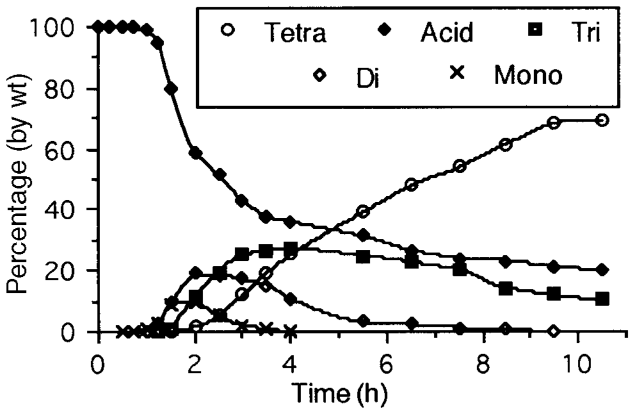


FIG. 2. Reaction profile (PE + C22:1).

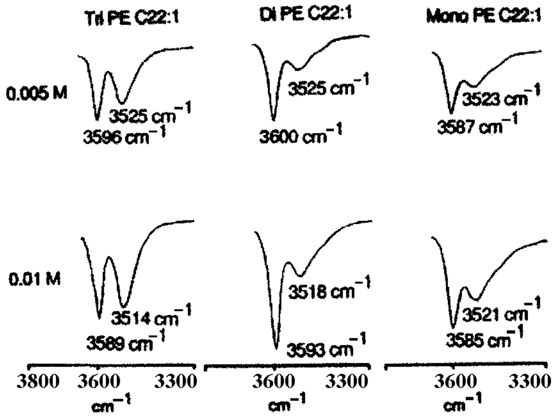


FIG. 5. OH stretching vibration of partial esters diluted in xylene.

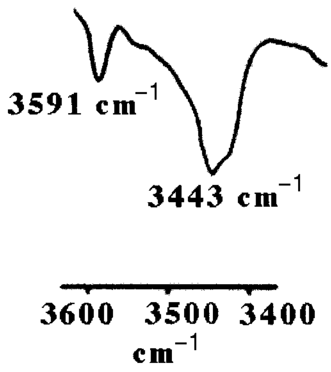


FIG. 3. OH Stretching vibration of erucic acid diluted in xylene (0.01 M).

crucial for lubricants, which are often required to perform under harsh conditions. We determined the onset temperature of weight loss of each compound (Fig. 7A and 7B) by thermogravimetry. The thermogravimetric curves are characteristic of a given compound, and the rates of these thermally induced processes are often a function of the molecular structure. The weight changes are the consequence of formation and cleavage of physical and chemical bonds at elevated temperatures.

The weight loss was observed under both helium and air. Under helium, we observed the effect of temperature alone to give a measure of thermal stability. Under air, oxidation reactions may take place and give rise to both thermal and oxidative degradation. Thermogravimetry provides useful information when combined with differential thermal analysis (DTA). Nearly all weight changes absorb or release energy and are thus measurable by DTA, whereas not all energy changes are accompanied by changes in weight. Weight loss can derive from two processes: degradation or evaporation. The DTA (heat flow) curve provides information on the nature of the weight loss. Figure 7A shows an endothermic peak, indicative of thermal decomposition, while the

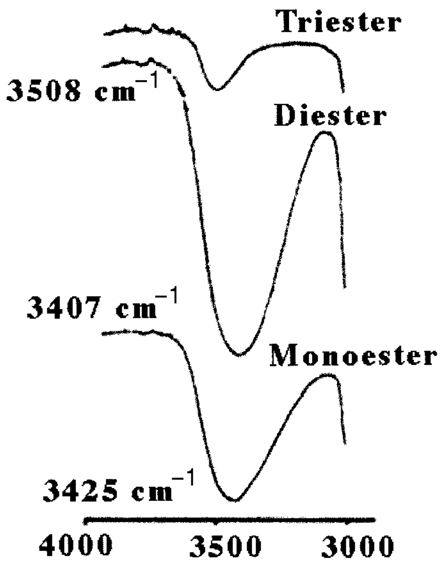


FIG. 4. OH stretching vibration of pure partial esters.

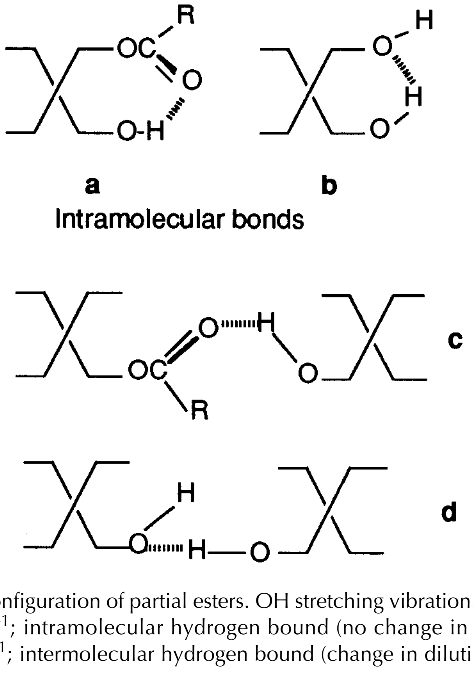


FIG. 6. Configuration of partial esters. OH stretching vibration: free OH, 3600 cm^{-1}; intramolecular hydrogen bound (no change in dilution), 3510 cm^{-1}; intermolecular hydrogen bound (change in dilution): 3400 cm^{-1}.

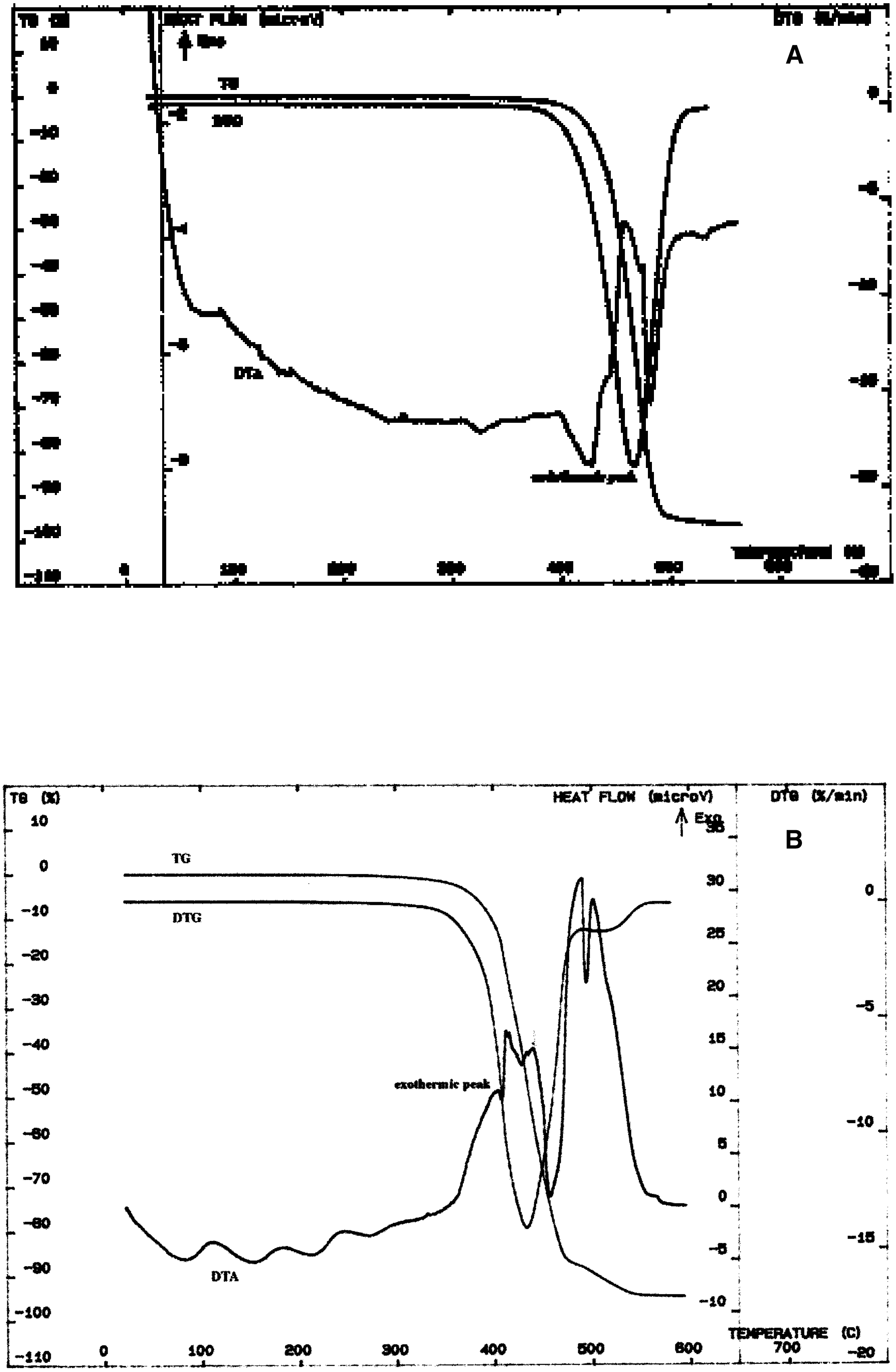


FIG. 7. (A) Thermogravimetric curves under helium (tetra PE22. (B) Thermogravimetric curves under air (tetra PE22).

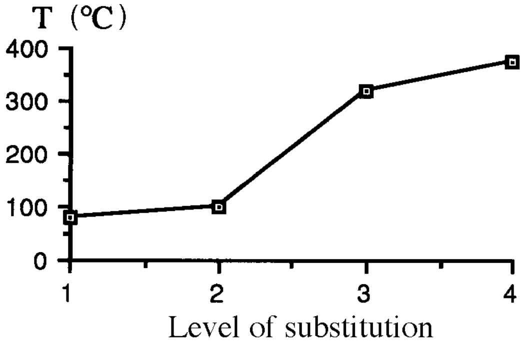


FIG. 8. Analysis under helium.

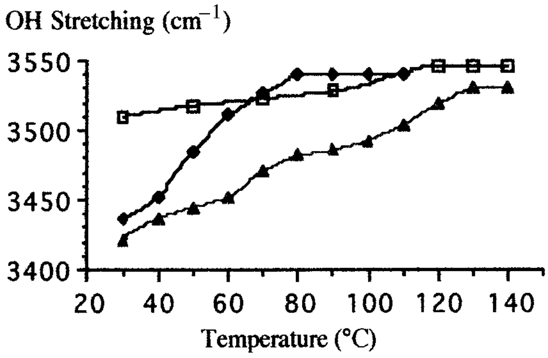


FIG. 10. OH stretching vibration. Influence of temperature on OH stretching vibration. □, Triester; ◆, diester; ▲, monoester.

exothermic peak in Figure 7B corresponds to oxidative degradation. The degradation peak and the weight loss occur at the same time, while evaporation is quite low. For the pentaerythritol esters, degradation is the main process because the neopentylpolyol esters are relatively nonvolatile.

With small amounts of compound, we were able to investigate the behavior of different esters as a function of temperature. If the weight loss (degradation or evaporation) occurs early, the compound would not be expected to be suitable as a lubricant. Plots (Figs. 8 and 9) of the temperature of weight loss as a function of the degree of substitution of the tetraol under helium and under air had similar shapes, although the degradation temperatures were lower under air. The tetraester gave the best results, and the mono- and diester the worst. The degradation temperature for the triester was quite high, even though somewhat less than for the tetraester. In general, stability fell with increasing number of remaining hydroxyl groups. The IR study provided further information on the structure–temperature relationships. Figure 10 shows the shift of the OH stretching vibration with increase in temperature from 30 up to 140°C. For the triester, the OH band shifted from 3510 to 3547 cm^{-1}, for the diester from 3436 to 3541 cm^{-1}, and for the monoester from 3422 to 3530 cm^{-1}. The change was greatest for the mono- and diesters. Because heat breaks intermolecular bonds, the OH stretching vibration shifts to a higher frequency. The structures of the mono- and diesters are thus more affected than that of triester, and these partial esters are consequently less stable than the tri- and tetraesters.

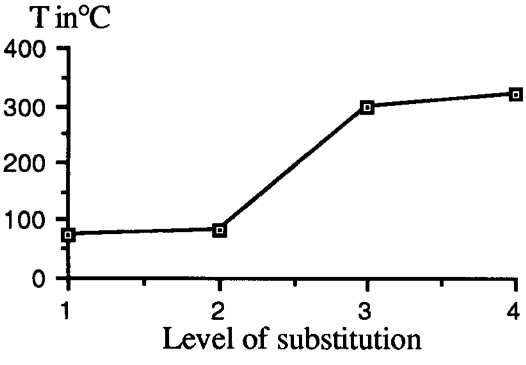


FIG. 9. Analysis under air.

The structure–property relationships can be summarized as follows: (i) the tetraester has a stable structure, with no free hydroxyl group. It has good high-temperature properties; and (ii) the triester with one free hydroxyl group underwent a small change in structure with rise in temperature. It has quite good high-temperature properties; and (iii) the mono- and diesters, with three and two remaining hydroxyl groups, respectively, underwent marked changes in structure with increase in temperature. They had poor high-temperature properties.

In conclusion, FTIR proved to be a valuable method for investigating the structures of the esters of pentaerythritol, in the pure state, and diluted in xylene, with increase in temperature. Analysis of the stretching frequency of the hydroxyl groups of the partial erucate of pentaerythritol and erucic acid provided information on the structure alterations on dilution in xylene and with increase in temperature. Erucic acid reacts in the dimer form (13), while the triester is less reactive than the two other partial esters, owing to the presence of intramolecular hydrogen bonds. The tetraester, with a stable structure, has good thermal stability. The triester had superior temperature behavior compared to the less stable mono- and diesters.

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