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Resistance of Polyfluorinated Complete Esters of Polyhydric Alcohols to Thermal Oxidation: Comparison with Nonfluorinated Analogs

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Abstract—Complete esters of pentaerythritol, trimethylolpropane, and 2,2-dimethyl-1,3-propanediol with polyfluorinated carboxylic acids were prepared by esterification. As determined by differential thermal gravimetric analysis in air, the resistance of the esters to thermal oxidation decreases in going from pentaerythritol derivatives to those of trimethylolpropane and then to those of 2,2-dimethyl-1,3-propanediol. The compounds synthesized surpass their nonfluorinated analogs in the resistance to thermal oxidation. **DOI:** 10.1134/S1070363206110223

Synthetic oils based on esters occupy leading positions on the world market of lubricants. The main representatives of these materials are esters of dicarboxylic acids, phosphoric acid, and polyhydric alcohols (polyols).

Recently polyol esters came into wide use in engineering thanks to the availability of the raw materials, simple production process, and valuable service characteristics.

The most important parameter in the estimation of the working characteristics of lubricants is their resistance to thermal oxidation. For lubricants based on esters, this parameter is largely determined by the steric structure of the acid or alcohol residues [1]. In particular, esters containing a quaternary carbon atom in the β position relative to the carboxy group are more stable thermally than esters without such atom.

This structural requirement is met by esters derived from pentaetythritol, trimethylolpropane, and 2,2-dimethyl-1,3-propanediol (neopentylene glycol).

The resistance to thermal oxidation of esters of pentaerythritol, trimethylolpropane, and neopentylene glycol with fatty acids has been studied in detail [2, 3]. The thermal stability of esters of polyols with fluorinated carboxylic acids, however, was not studied systematically.

It is known that esters of perfluorinated carboxylic acids and alcohols are chemically inert, highly stable, and nonflammable, which allows their use in sites of contact with potential oxidants [4]. Such lubricants become more versatile and can be used in cases when common oils are unsuitable.

In this study we examined how the structure of complete esters of polyfluorinated carboxylic acids and polyols (pentaerythritol, trimethylolpropane, neopentylene glycol) affects their resistance to thermal oxidation.

Esters of pentaerythritol (**I–III**), trimethylolpropane (**IV–X**), and neopentylene glycol (**XI–XVII**) were prepared by esterification of the polyols with polyfluorinated carboxylic acids in the presence of catalytic amounts of sulfuric acid (see scheme).

The esterification completeness and the structures of desired products I-XVII were checked by IR and NMR¹ (¹H, ¹⁹F) spectroscopy, elemental analysis, and determination of the ester numbers according to [5].

The IR spectra of compounds **I–XVII** all do not contain absorption bands of hydroxy groups, and the ester numbers determined by titration after hydrolysis of esters **I–XVII** are consistent with the calculated values. The physicochemical characteristics of **I–XVII** are given in Table 1, and the ¹H and ¹⁹F NMR data for **IV**, **V**, **VIII**, **XI–XIII**, and **XV–XVII**, in Table 2.

¹ Esters **I–III, VI, VII, IX, X**, and **XIV** are practically insoluble, which does not allow recording of their NMR spectra.

It should be noted that esterification of pentaerythritol with carboxylic acids yields a mixture of four compounds (from mono- to tetraesters). The most complete esterification of pentaerythritol is provided by carboxylic acid halides when used not only as esterifying agents, but also as the reaction medium (pentaerythritol : acid halide ratio 1 : 6). No additional catalyst is required in this case. After the reaction completion, excess polyfluoroacyl halide is removed from the reaction mixture (see Experimental). However, even this procedure allowed us to isolate with the required purity only esters I–III; all the other pentaerythritol derivatives were obtained as inseparable mixtures of mono-, di-, tri-, and tetra-esters.

Note that the thermal and thermal-oxidation stability of crude polyol esters largely depends on the catalyst used in their synthesis [4]. To eliminate the effect of the catalyst on the resistance to thermal oxidation,

Table 1. Yields and IR and analytical data for complete esters I-XVII

Comp. no.	Yield, %	bp, °C (<i>p</i> , mm Hg)	Ester number		ID anastrum	Found, %				Calculated, %		
			calculated	found	v[-O-C=O], cm ⁻¹	С	Н	F	Formula	С	Н	F
I	50	280-282(60)	42	40	1790	26.10	0.46	65.05	C ₃₃ H ₈ F ₅₂ O ₈	26.07	0.53	64.98
II	41	92 ^a	30	28	1789	25.01	0.38	61.77	$C_{41}H_8Cl_4F_{64}O_8$	24.29	0.41	61.22
III	53	226-228 (60)	29	27	1790	24.28	0.48	62.70	$C_{41}H_8F_{68}O_{16}$	24.04	0.39	63.07
IV	82	152–154 (5)	75	78	1780	30.08	1.62	55.27	$C_{18}H_{11}F_{21}O_6$	29.93	1.54	55.24
V	68	164–167 (5)	62	64	1781	29.12	1.32	58.76	$C_{21}H_{11}F_{27}O_6$	28.92	1.27	58.81
VI	67	213-215(5)	45	48	1785	27.44	0.99	63.58	C ₂₇ H ₁₁ F ₃₉ O ₆	27.66	0.95	63.20
VII	48	243-246(5)	36	38	1782	27.09	0.83	65.66	C ₃₃ H ₁₁ F ₅₁ O ₆	26.92	0.75	65.81
VIII	65	246-248(5)	47	46	1785	26.68	0.97	60.14	C ₂₇ H ₁₁ Cl ₃ F ₃₆ O ₆ ^b	26.55	0.90	55.98
IX	58	260–262(5)	40	39	1780	26.18	0.82	60.08	$C_{33}H_{11}Cl_{3}F_{48}O_{6}^{c}$	26.05	0.73	59.93
X	44	195–198 (5)	37	36	1789	25.33	0.79	61.96	C ₃₃ H ₁₁ F ₅₁ O ₁₂	25.27	0.71	61.78
XI	82	110–112(5)	117	113	1780	31.55	2.10	53.71	$C_{13}H_{10}F_{14}O_4$	31.47	2.03	53.60
XII	90	120–122 (5)	98	94	1780	30.34	1.77	57.54	$C_{15}H_{10}F_{18}O_4$	30.22	1.69	57.36
XIII	65	142–145 (5)	74	70	1781	28.47	1.31	62.35	C ₁₉ H ₁₀ F ₂₆ O ₄	28.66	1.27	62.04
XIV	48	153–155 (5)	59	56	1780	27.89	1.09	64.92	C ₂₃ H ₁₀ F ₃₄ O ₄	27.73	1.01	64.84
XV	53	165–167 (5)	68	68	1785	27.89	1.31	55.12	$C_{19}H_{10}Cl_2F_{24}O_4^{a}$	27.52	1.22	54.99
XVI	45	201-204(5)	56	55	1781	26.97	1.03	59.01	$C_{23}H_{10}Cl_2F_{32}O_4^{e}$	26.84	0.98	59.07
XVII	34	126–128 (5)	55	53	1790	26.21	1.02	60.98	$C_{23}H_{10}F_{34}O_8$	26.05	0.95	60.92
		1	1	1		1						1

^a Melting point. ^b Cl, found/calculated, %: 8.43/8.71. ^c Cl, found/calculated, %: 7.11/6.99. ^d Cl, found/calculated, %: 8.42/8.55. ^e Cl, found/calculated, %: 6.98/6.89.

Comp. no.	Formula	¹ H, ð, ppm	¹³ F, δ, ppm
IV	$^{1}_{CH_{3}CH_{2}C[CH_{2}OC(O)CF_{2}CF_{2}CF_{3}]_{3}}^{1}$	0.97 t (H ¹ , J _{1,2} 7.6 Hz), 1.60 q (H ²), 4.35 s (H ³)	81.84 m (F ^c), 120.32 m (F ^a), 128.00 (F ^b)
V	${}^{1}_{CH_{3}CH_{2}C}{}^{2}_{C}[CH_{2}OC(O)CF_{2}CF_{2}CF_{2}CF_{3}]_{3}$	0.96 t (H ¹ , $J_{1,2}$ 7.5 Hz), 1.60 q (H ²), 4.35 s (H ³)	82.02 m (F ^d), 115.58 m (F ^a), 124.67 m (F ^b), 127.13 m (F ^c)
VIII ^a	${}^{1}_{CH_{3}CH_{2}C}{}^{2}_{C}CH_{2}OC(O)CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CF_{2}CI]_{3}$	0.96 t (H ¹ , J _{1,2} 7.5 Hz), 1.59 q (H ²), 4.34 s (H ³)	70.11 t.m (F^{f} , $J_{f,c}$ 13.5 Hz), 119.62 m (F^{a}), 121.24 m (F^{c}), 122.32 m (F^{b} 122.75 (F^{d}), 123.69 (F^{e})
XI	$(CH_3)_2C[CH_2OC(O)CF_2CF_2CF_3]_2$	1.08 s (H ¹), 4.19 s (H ²)	81.92 m (F ^c), 120.54 m (F ^a), 127.96 (F ^b)
XII	$(\overset{1}{CH_3})_2\overset{2}{C}[CH_2OC(O)\overset{a}{CF_2}\overset{b}{CF_2}\overset{c}{CF_2}\overset{c}{CF_3}]_2$	1.08 s (H ¹), 4.19 s (H ²)	82.10 m (F ^d), 115.65 m (F ^a), 124.76 m (F ^b), 127.19 m (F ^c)
XIII ^a	$(CH_3)_2^2 C[CH_2OC(O)CF_2CF_2CF_2CF_2CF_2CF_2CF_3]_2$	1.07 s (H ¹), 4.19 s (H ²)	82.56 m (F ^f), 120.03 m (F ^a), 123.43 m (F ^c), 124.30 m (F ^{b,d)} , 127.87 m (F ^e)
XV ^a	$(\overset{1}{C}H_3)_2\overset{2}{C}[CH_2OC(O)C\overset{a}{F}_2C\overset{b}{F}_2C\overset{c}{F}_2C\overset{d}{F}_2C\overset{e}{F}_2C\overset{f}{F}_2CI]_2$	1.08 s (H ¹), 4.19 s (H ²)	69.06 t.m (F ^f , $J_{f,c}$ 13.7 Hz), 119.40 m (F ^a), 121.15 m (F ^c), 122.23 m (F ^b), 122.67 (F ^d), 123.63 (F ^e)
XVI ^a		1.07 s (H ¹), 4.19 s (H ²)	69.21 t.m (F ^h , $J_{h,e}$ 13.7 Hz), 119.57 t.m (F ^a , $J_{a,d}$ 11.4 Hz), 121.27 s (F ^c), 122.33 c (F ^b), 122.91 c (F ^{d,e,f}), 123.84 m (F ^g)
XVII	$ (CH_3)_2C[CH_2OC(O)CF(CF_3)OCF_2CF(CF_3)OCF_2CF_2CF_3]_2 $	0.97 s (H ¹), 3.40 s (H ²)	79.16 m (F ^{c,f}), 80.59 m (F ^{b,e}), 81.63 m (F ^h), 128.71 m (F ^g), 133.77 m (F ^a), 144.19 m (F ^d)

Table 2. ¹H and ¹⁹F NMR spectra of esters IV, V, VIII, XI-XIII, and XV-XVII

^a The ¹⁹F NMR data are presented taking into account data from [8, 9].

we additionally purified esters **I-XVII** by distillation in narrow temperature ranges.

The resistance of **I**–**XVII** to thermal oxidation was studied by thermal gravimetric analysis in air in the dynamic mode (5 deg min⁻¹). Three replicate runs were performed with each sample.

We revealed common features and differences in the resistance to thermal oxidation of fluorinated compounds I-XVII and esters of polyols with fatty acids; we also found how the degree of thermal degradation of I-XVII depends on the length of the acid residue and structure of the alcohol.

Comparative analysis of the resistance to thermal

oxidation was made in three groups of esters I-XVII differing in the structure of the acid moiety: esters with perfluoroalkyl (series A), ω -chloroperfluoroalkyl (series B), and perfluorodioxaalkyl (series C) groups (Table 3).

Previously Eychenne et al. [2] studied the thermal stability of complete esters of pentaerythritol, trimethylolpropane, and neopentylene glycol monopivalate with fatty acids in an inert atmosphere (He) and in air. They found that the thermal degradation of the compounds depended on the length of the acyl residue and structure of the alcohol. The longer the acid residue, the higher the degradation onset temperature of the ester; tetraesters of pentaerythritol appeared to be

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Series	Comp. no.		Interval of intense				
		1%	5%	10%	50%	100%	weight loss, °C
A	Ι	100	220	240	280	305	220–305
	IV	125	156	175	215	242	140-242
	V	115	166	180	222	255	140-255
	VI	165	210	230	270	300	200-300
	VII	210	243	255	298	320	230-320
	XI	85	115	125	165	190	100-190
	XII	110	132	150	190	215	120-215
	XIII	125	150	165	212	235	150-235
В	XIV	153	178	200	250	362	175-270
	II	210	290	315	355	475	270-370
	VIII	190	240	253	300	330	220-330
	IX	245	275	293	335	356	265-356
	XV	140	190	203	245	278	170-270
С	XVI	188	215	234	270	522	200-300
	III	150	212	230	275	305	212-305
	X	155	185	205	250	280	180-280
	XVII	93	125	140	170	220	120–220

Table 3. Results of differential thermal gravimetric analysis of I-XVII

more stable than triesters of trimethylolpropane and diesters of neopentylene glycol.

At the same time, within the groups of complete esters derived from the same polyhydric alcohols, certain derivatives did not differ significantly in the resistance to thermal oxidation. For example, the onset of the weight loss in the thermograms of complete esters of pentaerythritol and myristic (C_{14}), lauric (C_{12}), and pelargonic (C_9) acids was observed at 238, 232, and 235°C, respectively.

For the triesters of trimethylolpropane with the same acids, the onset of the weight loss in air was observed in the thermograms at the same temperature, about 220°C.

The respective temperatures for the neopentylene glycol diesters were 221, 215, and 215°C.

However, the resistance to thermal oxidation of the esters of all the three polyols with erucic (C_{22} , one double bond) and oleic (C_{18} , one double bond) acids was essentially different: decomposition onset temperature 320, 307, 308°C and 235, 221, 233°C, respectively.

Thus, a study of the resistance of complete esters of pentaerythritol, trimethylolpropane, and neopentylene glycol with fatty acids showed that, in going from a given compounds to its higher homolog, the increase in the thermal stability of esters is not sharp and becomes noticeable only when the difference in the chain lengths of the acyl residues is significant.

A different pattern is observed with fluorinated esters I-XVII.

Our choice of esters I-XVII was governed by the availability of polyfluoroalkanoic acids and was restricted to C_9 derivatives (except perfluorodioxaalkanoic acid derivatives of series C).

Our data on the resistance to thermal oxidation of trimethylolpropane triesters **IV–VII** and neopentylene glycol diesters **XI–XIV** (series A) show that, within each series A, the temperatures of the onset and end of thermal degradation grow with an increase in the acyl chain length (Table 3). In contrast to nonfluorinated analogs, the difference between the temperature points for the nearest homologs of series A, determined from the thermogravimetric curves of esters **IV–VII** and **XI–XIV**, is more significant, exceeding 10°C in all the cases.

The figure shows how the degradation onset temperature of trimethylolpropane triesters **IV–VII** and neopentylene glycol diesters **XI–XIV** depends on the length of the acyl group.² The onset point of the ther-

² The measurement results were treated by the least-squares method.

mal degradation is usually the temperature at which the weakest chemical bonds in the molecule are broken [6]. It is commonly believed that, in thermal degradation of esters, the primary event is cleavage of ester bonds. Actually the temperature at which the sample loses 5, 10, or 15% of its weight is arbitrarily chosen as the degradation onset temperature.

The figure shows that, with the same acyl groups, trimethylolpropane derivatives **IV–VII** are more stable, as in the case of nonfluorinated esters. The thermal stability of other complete esters of trimethylolpropane and neopentylene glycol can be estimated by extrapolation.

Note that, among complete perfluoroheptanoates I, VI, and XIII, pentaerythritol tetraester I is the most stable, which well correlates with the data of [2].

It is known that introduction of chlorine into various organic molecules enhances their thermal stability [7]. When studying thermograms of I-XVII, we also found that, at the same length of the acyl chain, esters II, VIII, IX, XV, and XVI prepared by esterification of pentaerythritol, trimethylolpropane, and neopentylene glycol with ω -chloroperfluoroalkanoic acids are more stable than esters of series A and C (Table 3). As for the influence of the structure of polyhydric alcohol on the resistance of esters II, VIII, IX, XV, and XVI to thermal oxidation, it is similar to that observed in [2] and in this study for esters of series A: Chlorinated tetraester II is the most stable, triesters VIII and IX are less stable, and diesters XV and XVI are the least stable.

Among the examined complete esters, compounds **III**, **X**, and **XVIII** are the least stable. This conclusion was based not only on the temperatures of 5% weight loss in thermogravimetric analysis. We also took into account the temperatures of complete burn-out of samples of **III**, **X**, and **XVII**.

Along with ester fragments, compounds III, X, and XVII contain ether bonds, and the polyfluorinated groups in them have a branched structure with two side trifluoromethyl groups. The structural features of III, X, and XVII are responsible for their decreased resistance to thermal oxidation. The revealed trends are similar to those observed with nonfluorinated esters. For example, Dufaure et al. [3] studied the resistance of octyl and 2-ethylhexyl oleates to thermal oxidation and found that the linear derivative was more stable than that with the side ethyl groups: The onset of weight loss was observed at 175 and 155°C, respectively.

Our results show that complete esters of pentaerythritol, trimethylolpropane, and neopentylene gly-



Temperature of the onset of the weight loss vs. length of the acyl residue: (1) complete trimethylolpropane esters **IV–VII** (y = 18.12x + 80.51, $R_{xy} = 0.996$) and (2) complete neopentylene glycol esters **XI–XIV** (y = 12.09x + 68.22, $R_{xy} = 0.995$).

col with polyfluorinated carboxylic acids exhibit higher resistance to thermal oxidative degradation than their nonfluorinated analogs. The difference between the nearest homologs of the polyfluorinated ester series in the degradation temperature is appreciably larger than for the nonfluorinated analogs.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer Spectrum One Fourier spectrometer in a thin layer for esters I and III–XII and in the diffuse reflection (DRA) mode for II. The ¹H and ¹⁹F NMR spectra were taken on a Bruker DRX 400 spectrometer in CDCl₃, internal references TMS and hexafluorobenzene, respectively. The ¹⁹F NMR chemical shifts are given relative to CFCl₃, with upfield shifts considered as positive. The differential thermal gravimetric analysis was performed on a Director-MOM device with programmed heating at a rate of 5 deg min⁻¹, at a sample weight of 100 mg and measurement error of 0.5%. Elemental analysis was performed on a CHN EA1108 Carlo Erba automatic analyzer.

Typical procedures for preparing esters I-XVII.

a. From polyol and fluoroalkanoic acid. To a mixture of 6.7 g of trimethylolpropane and 32.1 g of perfluorobutyric acid, heated to the melting point, 1 ml of sulfuric acid was added dropwise, after which the heating was continued for 2 h. The resulting mixture was washed with water, sodium carbonate solution, and again water, dried over CaCl₂, and distilled in an oil-pump vacuum; yield of ester **IV** 29.6 g (82%), bp 152–154°C (5 mm Hg). b. From polyol and fluoroalkanoic acid halide.³ To 13.6 g of pentaerythritol, 219.6 g of perfluoroheptanoyl fluoride was added dropwise at a rate at which the reaction mixture temperature did not exceed 55° C. After adding the whole amount of the fluoride, the mixture was heated at 140°C for 1 h. Excess acyl fluoride was distilled off, and the residue was distilled in an oil-pump vacuum; yield of ester II 76 g (50%), bp 280–282°C (60 mm Hg).

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³ Only for pentaerythritol tetraesters.