ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 7, pp. 1529–1534. © Pleiades Publishing, Ltd., 2011.
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Features of Reactions of Phthalic Anhydride with Polyfluorinated Alcohols

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Received June 22, 2010

Abstract—Polyifluoroalkyl mono- and diesters of phthalic acid were obtained by the reaction of phthalic anhydride with polyfluorinated alcohols. The structure of the polyfluoroalkyl phthalates was studied using IR and ^{1}H, ^{13}C NMR spectroscopy. The nature of the associative interactions between cyclohexanone and polyfluorinated alcohols was revealed.

DOI: 10.1134/S107036321107019X

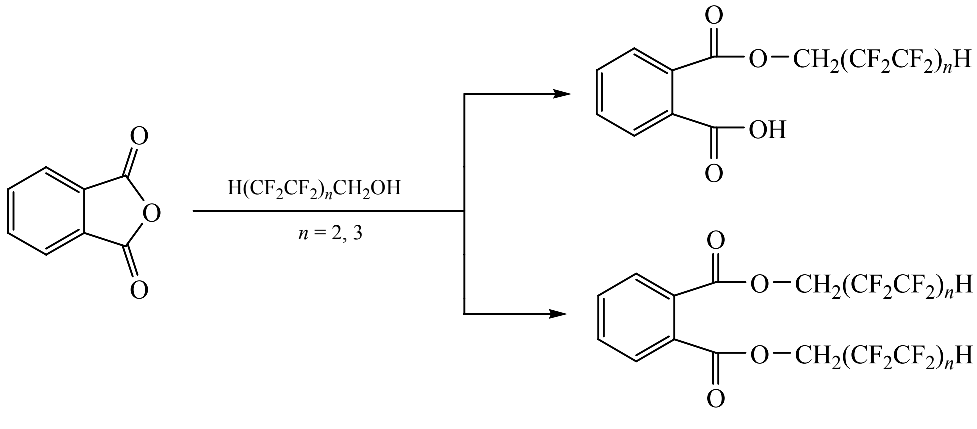
Phthalic anhydride is an important starting material for the production of various derivatives of phthalic acid, which are used in manufacturing paints, rubber products, plasticizers, etc. [1]. The introduction of various substituents in the benzene ring and in the chain component of the ester fragment gives rise to specific design of structures potentially appropriate for development of materials with different combinations of physical, mechanical and operational characteristics [2].

For introducing fluorine atoms in the benzene ring to obtain the corresponding derivatives of phthalic anhydride are known several methods [2–4]. However, it is interesting to obtain a phthalic acid ester conaining a polyfluorine fragment. The use of polyfluorinated compounds is very promising because they show enhanced hydrolytic stability, as well as the stability to light, heat and wear, and other useful properties inerent in polymeric materials due to the unique nature of polyfluorinated and perfluorinated groups [5–8].

The acylation by phthalic anhydride of polyfluorinated telomeric alcohols of the $H(CF_2CF_2)_n\cdot CH_2OH$ type with a degree of telomerization $n = 2, 3$ is unexplored because of the difficulty of formation of such esters in the classical esterification reaction, and therefore, it requires activating reagents [9].

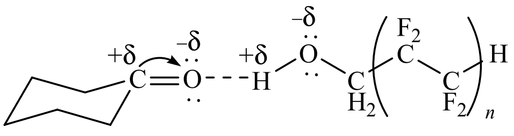
The aim of this work was to study the regularities at the obtaining phthalic esters with polyfluorinated alcohols in the medium of cyclohexanone, and the effect of the latter on the nature of associative interactions with polyfluorinated alcohols.

Synthesis of mono- and dipolyfluoroalkyl phthalates was performed according to the following reaction:



We found that phthalic anhydride does not react with a polyfluorinated alcohol to form ester in the temperature range 100–230°C for 2–6 h. This fact shows the low reactivity of the polyfluorinated alcohol in the reaction with phthalic anhydride because of their high acidity due to the presence of fluorine atoms possessing *–I* effect. In addition, phthalic anhydride is practically insoluble in polyfluorinated alcohols even at elevated temperatures.

Cyclohexanone, used as a medium for the acylation of polyfluorinated alcohols, provides favorable conditions for dissolving phthalic anhydride and ensuring the homogeneity of the esterifocation. The choice of cyclohexanone as a solvent is explained by the technological features of the acylation reaction: the cyclohexanone boiling point is 156.5°C [10], which allows to perform the esterification at an elevated temperature. Therewith, the structural features of the polyfluorinated alcohol, namely, the presence of proton-donor HCF_2 and HO groups, suggest a possibility of formation of its associates with cyclohexanone [11, 12]:



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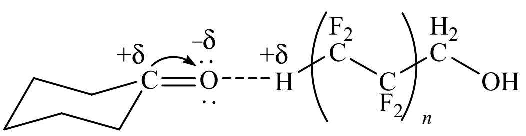

II

The electron density distribution in the appearing associate (**I**) contributes to the magnitude of the negative charge on the oxygen atom of the hydroxy groups of polyfluorinated alcohol and to an increase in its nucleophilic properties. Finally, this promotes attack of the electrophilic carbon atom of the carboxy group by the lone electron pair of the oxygen atom of the hydroxy group of the telomeric alcohol.

Thus, the role of cyclohexanone in the reaction of formation of polyfluoroalkyl phthalates consists not only in dissolving phthalic anhydride but also in the redistribution of electron density in the telomeric alcohol molecule through an associative interaction between the cyclohexanone and the polyfluorinated alcohol.

We found that with the increase in the length of perfluoroalkyl chain of the telomeric alcohol a regular almost twice decrease occurs in the degree of conversion of the initial reagents. As a rule, mono-polyfluoroalkyl esters are formed in higher yields and degree of conversion of the initial reagents, due, apparently, to steric hindrance to the esterification of the second carboxy group and low reactivity of the polyfluorinated alcohol. Interestingly, the lengthening of the polyfluorinated chain leads to a decrease in melting temperature of the formed ester, which is consistent with the data of a number of studies [13, 14].

Carrying out the reaction of acylation of polyfluorinated alcohols with phthalic anhydride in cyclohexanone medium at a temperature below 130°C leads to a significant decrease in the solubility of phthalic anhydride in the cyclohexanone and a decrease in the conversion of the reactants. It is important that raising the temperature of esterification to 150–200°C promotes intensive dehydrofluorination of perfluorinated chain and, consequently, the formation of resinous compounds, complicating isolation and purification of the reaction product.

We studied the possible associative interaction of polyfluorinated alcohol with the molecules of cyclohexanone and their influence on the strength of the hydrogen bonds in the associates formed in dilute solutions of carbon tetrachloride and chloroform by the methods of IR and ^1H NMR spectroscopy. In [15–17] a possibility has been considered of association of polyfluorinated alcohols with proton-acceptor amide groups in polycaprylamide, with acetone and with tertiary nitrogen atom of triethylamine.

In the IR spectra of polyfluorinated alcohols there are the bands of stretching vibrations ν_{OH} characteristic of the "free," that is, unbound hydroxy groups (monomers) and of those self-associated through intermolecular hydrogen bonds [17–19]. In the spectra of associates with cyclohexanone the absorption bands appeared characteristic of HO groups involved into the hydrogen bonding. It is interesting that the addition of cyclohexanone sharply increases the intensity of the polymer band and shifts it to lower wavenumbers. The data of IR spectroscopy of the non-associated telomeric alcohols and associated with cyclohexanone are given in Table 1. The value of $\Delta\nu$ shown in Table 1 is the difference between the frequencies of the

Table 1. Position of absorption band of the polyfluoroalcohol hydroxy group ν_{OH} in the IR spectra of monomers, polyassociates, and associates with cyclohexanone

System	Solvent	Concentration, M	Position ν_{OH}, cm^{-1}		In associaes with cyclohexanone	$\Delta\nu$, cm^{-1}
			monomer	polyassociation		
III	CCl_4	0.1092	3608	3460	–	148
	$CHCl_3$	0.0642	3604	3436	–	168
IV	CCl_4	0.1234	3582	3407	–	175
	$CHCl_3$	0.0824	3574	3390	–	184
III–cyclohexanone	CCl_4	0.0876 (**III**) 0.0831 (cyclohexanone)	–	–	3354	254
	$CHCl_3$	0.0898 (**III**) 0.0849 (cyclohexanone)	–	–	3315	289
IV–cyclohexanone	CCl_4	0.0972 (**IV**) 0.0864 (cyclohexanone)	–	–	3316	292
	$CHCl_3$	0.0996 (**IV**) 0.0888 (cyclohexanone)	–	–	3264	310

stretching vibrations of hydroxy groups in the monomer (the wavenumbers were obtained at the minimum allowable concentration of polyfluorinated alcohol in carbon tetrachlloride and chloroform) and the HO groups in the self-associates and associates with cyclohexanone.

As the data in Table 1 show, the solvent polarity plays an important role, and in more polar chloroform the formed hydrogen bonds are the most stable. The increase in the length of the perfluoroalkyl chain increases the strength of the polyfluorinated alcohol–cyclohexanone associates. These associates are more stable than, for example, the system of polyfluorinated alcohol–carboxylic acid amide, which indicates the possible additional associative interactions between fluorine and hydrogen atoms of the polyfluorinated alcohol with the cyclohexanone six-membered ring [11, 12, 17].

We studied a possibility of polyassociative interaction of polyfluorinated alcohol dissolved in carbon tetrachloride, as well as features of the association between the carbonyl group of cyclohexanone and protons of the telomereic alcohols by the method of ^{1}H NMR spectroscopy. For this purpose, the minimum allowable concentration of polyfluorinated alcohol in the carbon tetrachloride was determined, which allowed the comparison of the proton-donor activity of $H(CF_2CF_2)_n$ groups at various degrees of telomerization. The value of $\Delta\delta$ equal to the difference of proton chemical shifts of functional groups before and after adding the proton-acceptor cyclohexanone describes the ability to association of various proton-containing structural fragments of molecules, as well as the stability of the formed associates.

As show the data in Table 2, at a change in concentration from 0.177 to 0.354 mol l^{-1} the signal of the $H(CF_2CF_2)_n$ proton (n = 2,3) of the polyfluorinated alcohol does not undergo a shift to the strong or weak field. It appears as a triplet of triplets with characteristic chemical shift δ and the corresponding spin-spin coupling constants (^2J = 52 Hz, ^3J = 6 Hz) [19].

The data obtained by analysis of ^{1}H NMR spectra indicate a different associative ability of the proton of perfluoroalkyl chain of the telomeric alcohols to polyassociation. The increase in the number of fluorine atoms in the polyfluorinated alcohol molecule leads to reduced 1.2 times activity of polyassociate formation that is seen from the comparison of the $\Delta\delta$ for the singlet proton signal of HO groups at varying the polyfluorinated alcohol concentration in carbon tetrachloride. Probably, this result is associated with an increase in the size of the polyfluorinated alcohol molecule and steric barriers to these interactions.

Adding the proton-acceptor cyclohexanone in an appropriate quantity to the solution of polyfluorinated alcohol in carbon tetrachloride shifts the signals of the difluoromethyl group proton of the perfluoroalkyl

Table 2. Chemical shifts of the protons of $H(CF_2CF_2)_n$ and HO groups in the ^1H NMR spectra of polyfluorinated alcohol associates

Alcohol	Concentration, M	Polyassociates of polyfluorinated alcohol (CCl_4)			Associates through HCF_2CF_2 and HO groups of the polyfluorinated alcohols in CCl_4[a]			
		$\underline{H}CF_2CF_2$, δ, ppm	HO		$\underline{H}CF_2CF_2$		HO	
			δ, ppm	Δδ, ppm	δ, ppm	Δδ, ppm	δ, ppm	Δδ, ppm
III	0.177	5.88	2.16	0.25	6.03	0.15	4.06	1.9
	0.354	5.88	2.41					
IV	0.177	5.89	1.92	0.21	5.95	0.06	3.98	2.06
	0.354	5.89	2.13					

[a] Cyclohexanone concentration 0.0632 M.

chain and the HO group of the polyfluorinated alcohol downfield. It becomes possible to compare the proportion of associates **I** and **II**. Adding 0.0632 M of cyclohexanone reduces the proportion of the associative interaction of the $H(CF_2CF_2)_n$ proton 2.5-fold on going from the polyfluorinated alcohol with $n = 2$ to that with $n = 3$. Therewith, the proportion of associative interactions corresponding to the proton of HO group of the telomeric alcohol increases 1.1-fold. It is noteworthy that the strength of the associates of polyfluorinated alcohols with acetone is in fact 2-fold lower compared with the system of polyfluorinated alcohol-cyclohexanone [20], which is probably due to the molecular conformation of cyclohexanone providing more opportunity for the stabilization of the associative complexes of cyclohexanone-polyfluorinated alcohol through the formation of hydrogen bonds between hydrogen and fluorine atoms in the molecules of cyclohexanone and polyfluorinated alcohol, respectively. This conclusion is consistent with the above IR spectral features of these systems.

Thus, in dilute solutions of polyfluorinated alcohol and cyclohexanone the most favorable is the formation of associates with structure **I**, in which electron density distribution enhances nucleophility of the oxygen atom of HO group of the polyfluorinated alcohol and the possibility of acylation of the telomeric alcohol by phthalic anhydride.

EXPERIMENTAL

The IR spectra of the reaction products were recorded on a Specord-M82 device. The ^1H and ^{13}C NMR spectra were recorded at 25°C from solutions in deuterated dimethyl sulfoxide on a Varian Mercury-300 instrument at the operating frequency 300 MHz, internal reference tetramethylsilane. Individuality of the compounds obtained was confirmed by thin layer chromatography on the Sorbfil plates, eluent a mixture of diethyl ether and ethanol, 1:0.05. Development of the plates was performed using UV light. The melting points were determined on a Mettler Toledo instrument MP50 at a heating rate of 2°C min^{-1}. The IR spectra in the study of the associative interactions were taken from the solutions in chloroform and carbon tetrachloride in 0.4 mm cells of sodium chloride. The suspensions of phthalic anhydride and polyfluorinated alcohols in cyclohexanone were homogenized using a Prolabo ultrasonic bath at a frequency of 40 kHz.

Monopolyfluoroalkyl phthalates. Equimolar amounts of phthalic anhydride and polyfluorinated alcohol were preliminary dispersed in cyclohexanone in an ultrasonic field at a frequency of 40 kHz for 2 h at 70°C. Then the homogenized reaction mixture was maintained at 130°C for 2 h to complete transition of phthalic anhydride into the solution. The amount of the telomeric alcohol entered into reaction was evaluated by distilling off the unreacted polyfluorinated alcohol and cyclohexanone in a vacuum. Then the reaction mixture was washed with distilled water (50°C) to separate phthalic anhydride from the reaction product. The monoesters formed were purified by titration with 0.1 N sodium hydroxide solution until the transition of the monoesters in solution, and subsequent acidification with 0.1 N hydrochloric acid until the cessation of precipitation of the monoester crystals. The precipitated product was filtered off, washed with cold water and recrystallized from glacial acetic acid. The product was dried over magnesium sulfate.

1,1,5-Trihydroperfluoropentyl hydrogen phthalate. Colorless crystals. Yield 48.4%. Degree of the reactants conversions: phthalic anhydride 51%, polyfluorinated alcohol (*n* = 2) 67%, mp 101–103°C, R_f 0.81. IR spectrum, ν, cm^{-1} : 3598 (O–H), 2980–2914 (C–H), 1780 (C=O), 1684–1570 (C_{ar}–C_{ar}), 1216–1198 (CF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.938 m (1H, CH_2–CF_2, J = 14.1 Hz), 7,373 cyclohexanone (1H, CHF_2, ^2J = 50.1 Hz, ^3J = 5.7 Hz), 7.538–8.026 m (4H, C_6H_4), 12.778 (1H, COO H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 166.439 (1C, COOH), 128.847–133.963 (6C, C_6H_4), 62.034 (1C, $\underline{C}H_2CF_2$), 113.824–124.725 (4C, CF_2). Found, %: C 39.69, F 40.21. $C_{13}H_8O_4F_8$. Calculated, %: C 41.05, F 40.00

1,7,7-Trihydroperfluoroheptyl hydrogen phthalate. Colorless crystals. Yield 32.2%. Degree of conversion of the reactants: phthalic anhydride 42%, polyfluorinated alcohol (*n* = 3) 51%, mp 87–89°C, R_f 0.72. IR spectrum, ν, cm^{-1}: 3620 (O–H), 2982–2912 (C–H), 1785 (C=O), 1687–1572 (C_{ar}–C_{ar}), 1212–1200 (CF) . ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.961 m (1H, CH_2–CF_2, J = 14.1 Hz), 7.250 t.t (1H, CHF_2, ^2J = 50.4 Hz, ^3J = 5.4 Hz), 7.534–8.029 m (4H, C_6H_4), 12.431 (1H, COO H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 167.249 (1C, COOH), 127.621–133,113 (6C, C_6H_4), 62.047 (1C, $\underline{C}H_2CF_2$), 113.711–125.174 (6C, CF_2). Found, %: C 37.02, F 46.52. $C_{15}H_8O_4F_{12}$. Calculated, %: C 37.5, F 47.5.

Dipolyfluoroalkyl phthalates. Phthalic anhydride and polyfluorinated alcohol in molar ratio 1:2 respectively were preliminary dispersed in an ultrasonic field at a frequency of 40 kHz in the cyclohexanone medium for 2 h at 70°C. Then the homogenized reaction mixture was maintained at 130°C under vigorous stirring for 2 h to complete the phthalic anhydride transition into the solution. The amount of the telomeric alcohol entered into reaction was evaluated by distilling off the unreacted polyfluorinated alcohol and cyclohexanone in a vacuum. Then the reaction mixture was washed with distilled water (50°C) to separate phthalic anhydride from the reaction product. The purification of the dipolyfluoroalkylate formed was carried out by its recrystallization from glacial acetic acid. The product was dried over magnesium sulfate.

Di-(1,1,5-trihydroperfluoropentyl)phthalate. Colorless crystals. Yield 37.8%. Degree of the reactants conversion: phthalic anhydride 43%, polyfluorinated alcohol (*n* = 2) 52%, mp 84–86°C, R_f 0.88. IR spectrum, ν, cm^{-1}: 2962–2920 (C–H), 1804 (C=O), 1648–1528 (C_{ar}–C_{ar}), 1210–1150 (CF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.930 m (4H, CH_2CF_2, J = 14.7 Hz), 7,384 cyclohexanone (2H, CHF_2, ^2J = 50.1 Hz, ^3J = 5.6 Hz), 7.522–8.022 m (4H, C_6H_4). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 175.239 (2C, C=O), 134.841–132.867 (6C, C_6H_4), 60.198 (2C, $\underline{C}H_2CF_2$), 112.842–127.354 (8C, CF_2). Found, %: C 35.77, F 50.92. $C_{18}H_{10}O_4F_{16}$. Calculated, %: C 36.36, F 51.18.

Di(1,1,7-trihydroperfluorogeptyl) phthalate. Colorless crystals. Yield 24.5%. Degree of conversion of the reactants: phthalic anhydride 23%, polyfluorinated alcohol (*n* = 3) 31%, mp 64–66°C, R_f 0.75. IR spectrum, ν, cm^{-1}: 2968–2920 (C–H), 1792 (C=O), 1651–1518 (C_{ar}–C_{ar}), 1219–1157 (CF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.939 m (2H, C H_2CF_2, J = 14.7 Hz), 7.464 cyclohexanone (2H, CHF_2, ^2J = 50.1 Hz, ^3J = 5.4 Hz), 7.541–8.012 m (4H, C_6H_4). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 169.941 (2C, C=O), 133.811–132.823 (6C, C_6H_4), 62.338 (2C, $\underline{C}H_2CF_2$), 111.892–126.684 (12C, CF_2). Found, %: C 33.37, F 57.09. $C_{22}H_{10}O_4F_{24}$. Calculated, %: C 33.25, F 57.43.

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