Russian Journal of Applied Chemistry, Vol. 75, No. 7, 2002, pp. 1162–1165. Translated from Zhurnal Prikladnoi Khimii, Vol. 75, No. 7, 2002, pp. 1185–1188.

Polyfluoroalkyl Chlorosulfites as New Polyfluorinating Agents[1]

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Received January 17, 2002

Abstract—The interaction of polyfluorinated alcohols with triethylamine and the kinetics of the reaction of the resulting triethylamine complexes with thionyl chloride were studied, the mechanism of formation of polyfluoroalkyl chlorosulfites was considered, and the optimal reaction conditions were found. The alkylating power of polyfluoroalkyl chlorosulfites was studied in reactions with alkali metal halides (to obtain polyfluorohaloalkanes), in synthesis of acrylic and methacrylic acid esters, and in synthesis of polyfluoroalkyl ethers (with polyfluoroalkyl 1-adamantyl ethers as example).

Polyfluoroalkyl chlorosulfites have been studied poorly. These compounds were prepared by the reaction of perfluoroalkyl hypochlorites with thionyl chloride [1–5]

$$R_FOCl + SOCl_2 \rightarrow R_FOS(O)Cl + Cl_2.$$

In a later study [6], these compounds were prepared by the reaction of polyfluoro alcohols with thionyl chloride in the presence of triethylamine:

$$R_FOH + SOCl_2 \rightarrow R_FOSOCl.$$

In contrast to alkyl chlorosulfites, which are intermediates in reactions of alcohols with thionyl chloride and readily eliminate SO_2 to form chloroalkanes, polyfluoroalkyl chlorosulfites are stable compounds distillable without decomposition.

In this work, we studied the interaction of polyfluorinated alcohols with triethylamine and the reaction of the resulting complexes with thionyl chloride, with the aim to optimize the preparation of polyfluoroalkyl sulfites, which are of interest as polyfluorinating agents in syntheses of polyfluorohaloalkanes and of esters and ethers containing polyfluoroalkyl groups.

EXPERIMENTAL

Calorimetric studies were performed with a DAK-1-2M isothermal differential calorimeter. An ampule-in-ampule glass microreactor was placed in a calorimetric cell equipped with a device for breaking the inner ampule (a thin-walled sphere). After the required temperature was attained, the thin-walled sphere was broken, and the thermokinetic curve was recorded with an LKS 4003 device; this curve was processed to calculate the heat release rate and to determine the rate constants using the kinetic model. The heat of formation of the alcohol–triethylamine complex was determined in the bulk at 30°C and equimolar ratio of the alcohol and amine. Three replicate runs were performed, and the thermokinetic curves were processed by the trapezium method. The error of the calorimetric measurements was 3–5%.

The kinetics of formation of polyfluoroalkyl chlorosulfites was studied at 25, 30, and 35°C. The initial concentrations of the alcohol–amine complex and thionyl chloride were 0.18 M.

Procedures for synthesis and identification of polyfluoroalkyl chlorosulfites are reported elsewhere [7]. The reaction was performed in chloroform; the complex of a polyfluorinated alcohol (0.05 mol) with triethylamine (0.05 mol) was added to a solution of 0.075 mol of thionyl chloride, cooled to –40°C; in the process, the mixture was not allowed to warm up above –15°C. After adding the whole amount of the complex, the mixture was warmed up to 20°C. The precipitate of triethylamine hydrochloride was filtered off, excess thionyl chloride was distilled off at atmospheric pressure, and the residue was vacuum-distilled. The yields and constants of polyfluoroalkyl chlorosulfites obtained by the reaction

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[1] Reported at the 3rd International Conference “Chemistry, Technology, and Applications of Fluoro Compounds” (St. Petersburg, July 6–9, 2001).

Table 1. Physicochemical characteristics of polyfluoroalkyl chlorosulfites $H(CF_2CF_2)_nCH_2OS(O)Cl$

n	Yield, %	Empirical formula	bp, °C/P, mm Hg	d_4^{20}, g cm^{-3}	n_D^{20}
1	84.2	$C_3H_3F_4SO_2Cl$	61/40	1.611	1.3704
2	82.0	$C_5H_3F_8SO_2Cl$	99/50	1.783	1.3580
3	80.0	$C_7H_3F_{12}SO_2Cl$	101/10	1.787	1.3428

$$H(CF_2CF_2)_nCH_2OH \cdot N(C_2H_5)_3 + SOCl_2$$

$$\rightarrow H(CF_2CF_2)_nCH_2OSOCl + (C_2H_5)_3N \cdot HCl, \quad n = 1\text{–}3,$$

are listed in Table 1.

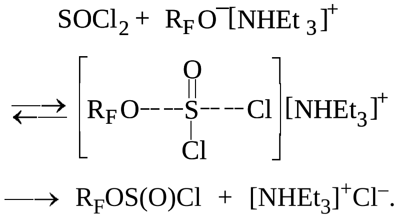
Polyfluorinated alcohols virtually do not react with thionyl chloride in the absence of triethylamine. If triethylamine is added to a mixture of alcohol and thionyl chloride, the yield of alkyl chlorosulfite does not exceed 15%. The highest yield (80–84%) is attained when the complex of a polyfluorinated alcohol with triethylamine, prepared in advance, is added to thionyl chloride. Therefore, using microcalorimetry and IR and ^{1}H NMR spectroscopy, we studied the interaction of polyfluorinated alcohols with triethylamine.

The thermal effect of the interaction of polyfluorinated alcohols with triethylamine was estimated microcalorimetrically. The heat of interaction with triethylamine is 19.9 kJ mol^{-1} for 2,2,3,3-tetrafluoro-1-propanol (FA1) and 20.7 kJ mol^{-1} for 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (FA2).

Complexation causes significant changes in the IR spectra of polyfluorinated alcohols. The stretching vibration band of the OH group at 3620 cm^{-1} sharply decreases in intensity, and a new medium-intensity band appears at 2600–2700 cm^{-1}, which is split in several bands (Fig. 1). These changes are due to formation of a salt, $H(CF_2CF_2)_nCH_2O^- \, ^+NH(C_2H_5)_3$.

The conclusions made from the IR spectra are confirmed by the ^{1}H NMR spectra of FA2 solutions in CCl_4. Interaction of FA2 with triethylamine causes a downfield shift of the hydroxyl proton signal by 2.49 ppm. Triethylamine is a stronger proton acceptor than acetone, as with acetone, under similar conditions, the OH proton signal is shifted downfield by only 1.86 ppm. Thus, the complexation is favored by the acid properties of polyfluorinated alcohols and high basicity of triethylamine.

Based on the data on complexation with triethylamine, we optimized the conditions for preparing polyfluoroalkyl chlorosulfite. We suggest the following mechanism of nucleophilic substitution of chlorine in the thionyl chloride molecule:



$$SOCl_2 + R_FO^-[NHEt_3]^+ \rightleftarrows \left[R_FO\text{---}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Cl}{|}}{S}}\text{---}Cl\right][NHEt_3]^+ \longrightarrow R_FOS(O)Cl + [NHEt_3]^+Cl^-.$$

This mechanism is confirmed by the kinetic data. Using the kinetic model, we processed experimental heat release curves [8] and determined the rate constants and the effective activation energy of the reaction. For the reaction of thionyl chloride with FA1–triethylamine, the second-order rate constants are as follows (l mol^{-1} s^{-1}): 0.020 at 25°C, 0.025 at 30°C, and 0.027 at 35°C. The effective activation energy is 31.77 kJ mol^{-1}.

We have studied the alkylating power of polyfluo-

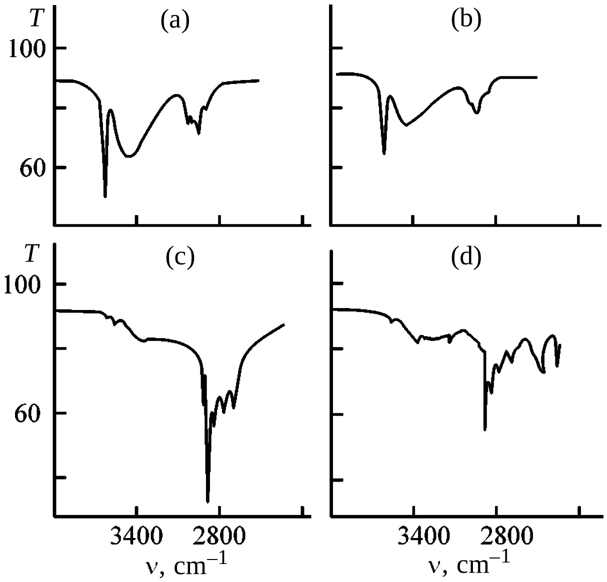


Fig. 1. IR spectra in CCl_4 of (a, b) 2,2,3,3-tetrafluoropropanol and (c, d) 1 : 1 2,2,3,3-tetrafluoropropanol–triethylamine complex. Cell thickness 0.18 mm. (T) Transmission and (ν) wave number. Concentration, M: (a, c) 0.4 and (b, d) 0.2.

Table 2. Polyfluoroalkyl acrylates and methacrylates

R	*n*	Yield, %	bp, °C/*P*, mm Hg	d_4^{20}, g cm^{-3}	n_D^{20}
H	1	76.2	56/60	1.2860	1.3666
		34.0*	75/110	1.2858	1.3668
H	2	76.0	85/40	1.4460	1.3462
		38.5*	84/40	1.4884	1.3460
H	3	76.1	110/40	1.5802	1.3402
		45.2*	107/40	1.5974	1.3400
CH_3	2	76.4	100/40	1.4210	1.3578
		56.0*	87/40	1.4106	1.3580
CH_3	3	76.5	104/20	1.5360	1.3506
		50.8*	112/40	1.5390	1.3500

* Data of [9].

Table 3. Polyfluoroalkyl 1-adamantyl ethers Ad–$OCH_2(CF_2CF_2)_nH$

n	Yield, %	bp, °C/*P*, mm Hg	n_D^{20}	Analytical data, %*		
				C	H	F
1	76	86/2	1.4440	$\frac{58.02}{58.65}$	$\frac{6.70}{6.77}$	$\frac{28.21}{28.57}$
2	75	106/2	1.4233	$\frac{49.00}{49.20}$	$\frac{4.60}{4.92}$	$\frac{41.03}{41.53}$

* Numerator: found; denominator: calculated.

roalkyl chlorosulfites in the reactions with alkali metal halides, carboxylic acid salts, and alcohols.

Polyfluoroalkyl chlorosulfites react with alkali metal halides (KF, LiCl, KBr, KI) in diethylene glycol to form the corresponding polyfluorohaloalkanes in 75–90% yield:

$$H(CF_2CF_2)_nCH_2OS(O)Cl + MX \rightarrow H(CF_2CF_2)_nCH_2X + MCl + SO_2,$$

where $n = 1, 2, 3$; X = F, Cl, Br, I; M = K, Li, Na.

The advantages of the synthesis of polyfluorohaloalkanes by substitution of the chlorosulfite group in alkyl chlorosulfites are the use of low-toxic chemicals, versatility, and high yield of the reaction products.

By the reaction of alkyl chlorosulfites with potassium (meth)acrylate, we prepared the corresponding polyfluoroalkyl (meth)acrylates:

$$CH_2{=}C(R)COOH + H(CF_2CF_2)_nCH_2OS(O)Cl \longrightarrow CH_2{=}C(R)COOCH_2\text{–}(CF_2CF_2)_nH,$$

where $n = 1, 2, 3$; R = H, CH_3.

The yield of acrylates and methacrylates in this case is appreciably higher than in the known procedure [9] (Table 2).

Polyfluoroalkyl chlorosulfites readily react with alcohols in dioxane to form the corresponding ethers. For example, previously unknown polyfluoroalkyl 1-adamantyl ethers were prepared by the reaction of 1-adamantol with polyfluoroalkyl chlorosulfites:

$$\text{Ad–OH} + H(CF_2CF_2)_nCH_2OS(O)Cl \longrightarrow \text{Ad–}OCH_2(CF_2CF_2)_nH,$$

where $n = 1, 2$.

Adamantyl polyfluoroalkyl ethers are colorless liquids readily distillable in a vacuum (Table 3). The composition and structure of these compounds were determined by elemental analysis and by IR and ^1H NMR spectroscopy.

The IR spectra of the ethers exhibit a very strong absorption at about 2916 cm^{-1} assigned to the stretching vibrations of the methylene and methine groups and at about 1124 cm^{-1} assigned to the ether C–O stretching vibrations.

The ^1H NMR data for 1-adamantyl alkyl ethers are given in Table 4.

The ^1H NMR spectra of 1-[2,2,3,3-tetrafluoropropoxy]adamantane and 1-[2,2,3,3,4,4,5,5-octafluoropentoxy]adamantane contain characteristic proton signals of the adamantane moiety [10]. The β- (δ 1.56 ppm) and δ-protons (δ 1.68 ppm) give narrow signals. The signal of the γ-protons is broad (δ 2.12 ppm). The signal of the methylene protons in the polyfluoroalkyl moiety is a triplet with a coupling constant of 12 Hz. The proton signal of the hydrofluoromethyl group is a triplet of triplets with a coupling constant of 6 Hz.

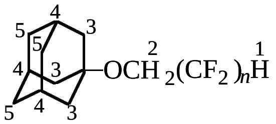
According to the predictions of the medicobiological activity, perfluoroalkyl 1-adamantyl ethers show promise as antidepressants and tranquilizers.

CONCLUSIONS

(1) A procedure was developed for synthesis of polyfluoroalkyl chlorosulfites by the reaction of thionyl chloride with complexes of polyfluorinated alcohols with triethylamine.

(2) Complexation in the system polyfluorinated alcohol–triethylamine was studied by microcalorimetry and IR and ^1H NMR spectroscopy, and the saltlike structures of the complexes were suggested.

Table 4. ^{1}H NMR spectra of 1-adamantyl alkyl ethers



n	Chemical shift δ, ppm					Coupling constant, Hz		
	1	2	3	4	5	J_{HCF}	J_{HCCF}	J_{2HCH}
2	5.78 t.t	3.64 t	1.56 s	2.12 s	1.66 s	52	6	12
4	5.84 t.t	3.74 t	1.56 s	2.12 s	1.68 s	52	6	12

(3) A mechanism of formation of polyfluoroalkyl chlorosulfites was suggested, involving bimolecular nucleophilic substitution of chlorine by the polyfluoroalkoxy group in thionyl chloride in its reaction with the polyfluorinated alcohol–triethylamine complex.

(4) Polyfluoroalkyl chlorosulfites efficiently alkylate carboxylic acid salts (alkyl acrylates and methacrylates were obtained) and alcohols (with 1-adamantol as example); they can also be used for preparing polyfluorohaloalkanes by the reactions with metal halides.

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