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Kinetics and Mechanism of Reaction between Polyfluorinated Alcohols and Thionyl Chloride

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Abstract —Complexing of polyfluorinated alcohols with triethylamine was studied by means of microcalorimetry, IR and NMR spectroscopy. The reaction kinetics of these polar complexes with thionyl chloride was investigated using calorimetry of heat fluxes applying mathematical simulation procedure. The second order of nucleophilic substitution reaction of chlorine by polyfluoroalkoxy group was established.

We reported formerly [1] on reaction of telomeric polyfluorinated alcohols with thionyl chloride affording polyfluoroalkyl chlorosulfites.

$$\underset{\textbf{I, II}}{H(CF_2)_nCH_2OH{\cdot}NEt_3} + SOCl_2 \rightarrow \underset{\textbf{III, IV}}{H(CF_2)_nCH_2OS(O)Cl} + Et_3N{\cdot}HCl$$

$$n = 2\ (\textbf{I, III}),\ 4\ (\textbf{II, IV})$$

This study was aimed at investigating the kinetics and features of triethylamine complexing with the polyfluorinated alcohols that determined the course of reaction.

We established that application of a preliminary prepared equimolar complex triethylamine–alcohol **I, II** ensured preparation of polyfluoroalkyl chlorosulfites **III, IV** in a 84% yield. These results were obtained in the study on the effect of the reagents mixing order (Table 1). Apparently the increase in the yield originated from the formation of H-complexes between alcohols **I, II** and triethylamine that enhanced the alcohol tivity toward the thionyl chloride. Therefore the complexing of polyfluorinated alcohols **I, II** with triethylamine was studied by means of microcalorimetry, IR, and ^{1}H NMR spectroscopy. The microcalorimetry measurements made it possible to evaluate the heat evolution and the time of complexing process. The heat evolution during the interaction of the triethylamine with alcohol **I** was 19.9 kJ mol^{-1} (at 303 K), with alcohol **II** 20.7 kJ mol^{-1}. The experimental data obtained may be rationalized on assumption that alcohols **I, II** apparently form strong hydrogen bonds with triethylamine for the polyfluorinated alcohols possess enhanced acidity which determine their proton-donor ability. The acidity of alcohols **I, II** depends on the acidity of HO– and HCF_2– groups. The specific features of the part played by these groups in the association we studied by means of IR and ^{1}H NMR spectroscopy.

The structures of polyassociates of polyfluorinated alcohols were studied before [2], and linear and cyclic polyassociates were suggested to arise due to hydrogen bonds formation involving hydroxy and difluoromethyl groups.

Table 1. Effect of reagents mixing order in reaction of $H(CF_2)_nCH_2OH$ with $SOCl_2$ in the presence of triethylamine on the yield of polyfluoroalkyl chlorosulfites (**III, IV**)

Alcohol *n*	Order of reagents mixing	Yield of compounds (**III, IV**), %
2	$SOCl_2$ + alcohol	5
2	$SOCl_2$ + complex alcohol–amine, 1:1	84
2	Alcohol + $SOCl_2$ + amine	15
4	$SOCl_2$ + alcohol	5
4	$SOCl_2$ + complex alcohol–amine, 1:1	82
4	Alcohol + $SOCl_2$ + amine	16

Table 2. Stretching vibrations of functional groups in the IR spectra of 2,2,3,3-tetrafluoropropan-1-ol (**I**), cm^{-1}

Functional groups	**I**			**I** + Et_3N, solution in CCl_4	
	Liquid film	Solution in CCl_4			
		0.4 M	0.2 M	0.4 M	0.2 M
OH	3620 m	3620 m	3620 m	3620 w	3620 w
	3380 m.br	3461 m	3478 m.br	3426 w.br	3444 w.br 3382 w 3320 w 3223 w
F_2C–H	3003 m	3020 m	3020 m	3012 m	3012 w

The complexing features were estimated by changes in the region of stretching vibrations of the hydroxy and difluoromethyl groups comparing the IR spectra recorded from liquid films, alcohol solutions in tetrachloromethane (0.2 and 0.4 M), and solutions of the complex alcohol–amine of the same concentration. Also an appearance of new absorption bands in the region 2588–2800 cm^{-1} was observed (absorption in this part of IR spectrum was not observed for triethylamine) (Table 2). The comparison of the IR spectra showed that, firstly, in the region of the stretching vibrations of the hydroxy group the band widened and its intensity decreased, the band at 3620 cm^{-1} was weakly pronounced, and the bands at 3426 cm^{-1} (in 0.4 M solution) and 3444 cm^{-1} (in 0.2 M solution) became very wide and weak. Secondly, a new band of medium intensity appeared in the region of 2800 cm^{-1} that in the dilute solution (0.2 M) split into a set of bands. The appearance of this band and the sharp weakening of the hydroxy group band may be rationalized assuming formation of triethylammonium cations that possess absorption bands in the region 2800–2300 cm^{-1} [3] and are involved into a salt-like structure.

$$HCF_2CF_2CH_2OH + N(C_2H_5)_3 \rightarrow HCF_2CF_2CH_2O^{-}\,{}^{+}NH(C_2H_5)_3.$$

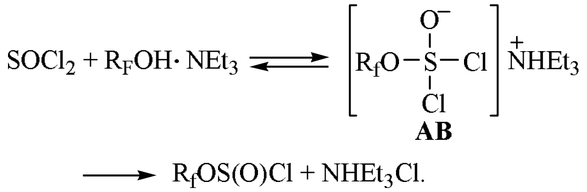
Similar trends were also observed for the complexing in the system 2,2,3,3,4,4,5,5-octafluoropentan-1-ol–triethylamine.

The high proton-donor ability of the polyfluorinated alcohols is due to the presence of a labile hydrogen of the hydroxy group capable of complex formation with carbonyl, amino, and amido groups that is easily detected in the NMR spectra by the change of the position and pattern of the hydroxy group proton signal [4]. We expected that the complexing of the polyfluorinated alcohol with the triethylamine would be also observed in the ^1H NMR spectra of the system under study.

We compared the location of proton signals from the hydroxy and difluoromethyl groups of alcohol **II** in the following systems: (1) the alcohol solution in tetrachloromethane (with chloroform added as "marker") of 0.173 and 0.346 M concentrations; (2) the same solutions with addition of an equimolar amount of acetone; (3) triethylamine solution with addition of an equimolar amount of alcohol in tetrachloromethane (in the presence of chloroform) of 0.1 M concentration.

On adding into the system of acetone as proton-acceptor associates form involving hydrogen atoms of HO–, H–CF_2–, and $HCCl_3$ groups as show the downfield shifts of proton signals belonging to these groups. The proton of the difluoromethyl group interacted stronger with the carbonyl oxygen than the proton of the chloroform: $\Delta\delta$(H–CF_2) was 0.08, and $\Delta\delta$($HCCl_3$) was 0.04 ppm. The interaction with the hydroxy group proton is more pronounced: $\Delta\delta$ 1.86 ppm. The pattern in the system alcohol **II**–triethylamine is unlike that of the system alcohol **II**–acetone: The interaction with difluoromethyl group is weaker, but the associative interaction of the hydroxy group proton with the unshared electron pair of the nitrogen in the triethylamine is much stronger: $\Delta\delta$(HO) 2.49 ppm in the system alcohol **II**–triethylamine, and 1.86 ppm in the system alcohol **II**–acetone. Thus the high polarization of the oxygen–hydrogen bond in the complexes alcohol–amine revealed by the analysis of ^1H NMR spectra, the involvement of difluoromethyl group into the associative interaction alongside the data of studies with the use of IR spectra showed that the interaction of polyfluorinated alcohol with amine resulted in a complicated system of polar molecular complexes.

The alcohol reaction with the thionyl chloride furnishing alkyl chlorosulfites may be regarded as a nucleophilic attack of the alcohol molecule on the electron-deficient sulfur atom. In contrast to a saturated carbon atom the nucleophilic substitution at the sulfur atom of the thionyl chloride is facilitated by existence of unoccupied *d*-orbitals favoring activated complex formation and the reaction proceeding along the S_N2 mechanism [5]. Thus the reaction of polyfluorinated alcohol **I, II** with triethylamine resulted in H-complexes that reacted with thionyl chloride through a polar intermediate **AB** which dissociated further into a polyalkyl chlorosulfite and triethylammonium chloride.



$$\mathrm{SOCl_2 + R_FOH\cdot NEt_3} \rightleftharpoons \left[\mathrm{R_fO{-}\overset{O^-}{\underset{Cl}{S}}{-}Cl}\right]\overset{+}{\mathrm{N}}\mathrm{HEt_3} \longrightarrow \mathrm{R_fOS(O)Cl + NHEt_3Cl.}$$

AB

To confirm the suggested mechanism we carried out kinetic measurements. The kinetics of polyfluoroalkyl chlorosulfites **III, IV** formation resulting from thionyl chloride reaction with complexes of alcohols **I, II** with triethylamine were studied by the method of heat flux calorimetry [6]. The experiments showed that the thionyl chloride reacted with the complex alcohol **I, II**–amine rather fast, irreversible, and no side products formed under the run conditions as proved by IR spectra of the reaction mixture. Therefore the calorimetry of heat flux proved to be a convenient method for the kinetic study providing a possibility of direct measurement of heat evolution rate as a function of time $W^e = f(\tau)$. The estimation of kinetic parameters from the indirect experiments on the heat evolution rate in the course of the reaction requires solution of two problems.

The first problem consists in the interpretation of the instrument readings and their recalculation into a physical value of heat evolution rate.

The second problem includes a building up of the process model and in evaluation of this model parameters basing on the experimental data. The mathematical simulation consists virtually in the search for a model giving the best fit to the experimental data and to the general concepts concerning the nature of the reactions under study. The software system corresponding to the above described calculation procedure was realized in the *Delphy* medium.

The reaction of the alcohol with thionyl chloride can be expressed as two consecutive reactions A+B - AB > D + C. The first stage of complex **AB** formation is reversible, but we have taken into account a simpler model containing only a direct reaction for the contribution of the reverse reaction is negligible due to the high rate of the subsequent transformation of **AB** into the final reaction products, and then at the equal initial concentrations of the thionyl chloride **A** and alcohol complex with amine **B** the kinetic model is as follows:

$$\frac{dC_\mathrm{A}}{d\tau} = -k_1C_\mathrm{A}^2$$

$$\frac{dC_\mathrm{AB}}{d\tau} = k_1C_\mathrm{A}^2 - k_2C_\mathrm{AB}$$

For all experiments carried out at different temperatures the adequacy dispersion for the chosen model was within the limits of 1%, and evaluation error for the constants was 10–12%. Due to small temperature range in the experiment and low sensitivity of the reaction to the changes in temperature the calculated constants have close values (the discrepancies in the values are within the tolerable range). Therefore the results of simulation according to the given equations in the temperature range 25–35°C may be presented as two constants: k_1 0.02± 0.003 l (mol s)$^{-1}$ and k_2 0.03 ± 0.003 s^{-1}.

Into the software system the other models were also included : a model where both reactions had tentative reaction order that required determination, and models including reverse and autocatalytic reactions. All the models were tested for obtaining the most reliable results. The model describing the reaction proceeding along bimolecular mechanism gave the best fit to the experimental data among thirteen models.

The kinetic studies performed suggest that the reaction between the alcohol–amine complex and thionyl chloride follows the S_N2 mechanism.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord M-82 using a cell 0.18 mm thick. ^{1}H NMR spectra were registered on spectrometer Tesla BS487 (100 MHz, internal reference TMS).

The synthesis and identification of compounds **III, IV** was described in [1]. Compounds **III, IV** were prepared by reaction of a complex alcohol **I, II**–triethylamine, 1:1, with 1.5-fold excess of thionyl chloride at –5°C.

The calorimetric studies were performed using an isothermal differential calorimeter DAK-1-2M. A glass microreactor of the “ampule within ampule” type was placed into the calorimetric cell, after attaining the chosen constant temperature the glass ball with thin walls was crushed, and the thermokinetic curve was recorded by an automatic recorder LKS-4-003. The heat evolution rate was evaluated by treating the latter curves.

The heat of formation for the complex complex alcohol–triethylamine was performed at 30°C without solvent, at the molar ratio alcohol–amine 1:1. Three repeated runs were carried out, the thermochemical curves were treated by trapezoid rule. The accuracy of the kinetic measurements was within 3–5%.

The kinetics of compounds **III, IV** formation was measured at 25, 30, 35, and 40°C, the initial concentrations of the complex alcohol **I, II**–amine and thionyl chloride were 0.18 mol l^{-1}. The error in estimation of the kinetic parameters was 1–12%.

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