

Catalytic Fluorodechlorination of Polychlorofluorobenzenes with Potassium Fluoride

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Abstract—Fluorodechlorination of polychlorofluorobenzenes with potassium fluoride in the presence of phase-transfer catalysts was investigated. "Onium" catalysts [hexaethylguanidinium chloride, tetra(diethylamino)phosphonium bromide] take part in the stabilization of the intermediate σ -complex. Catalytic role of polyethers (tetraglyme, 18-crown-6) in the fluorodechlorination process is limited to increasing the fluoride ion concentration.

Application of phase-transfer catalysts is among the most efficient methods for activation of halogen exchange in fluorination of chloroaromatic compounds with alkali metal fluorides [1–3].

In practice, the most interesting operation mode is the use of phase-transfer catalysts without solvents. In this case is no need of reaction products isolation from the solvent, and also of recovery of the latter.

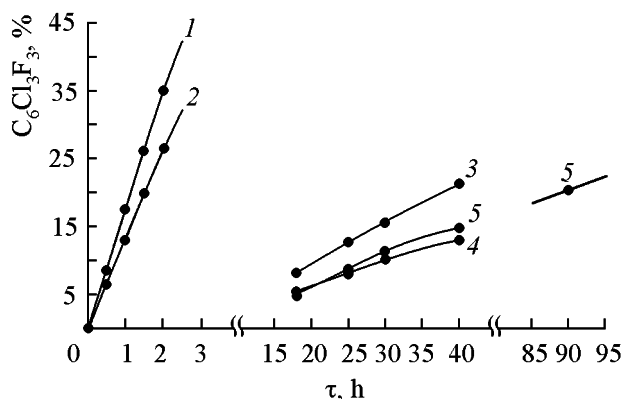
Obviously, the practically important catalysts beside being efficient should possess some other characteristics: a high stability under the synthesis conditions, availability and not too high price. These requirements are met by quaternary phosphonium

salts, guanidinium derivatives, polyethylene glycol alkyl ethers, and crown-ethers. The present study concerns the catalytic activity of these phase-transfer catalysts in the absence of solvents.

According to modern views the fluorodechlorination of chloroaromatic compounds with potassium fluoride occurs both on the surface of the solid phase and in the ω -phase, directly contiguous to the potassium fluoride surface [4]. In both cases the catalyst effect is ascribed to increasing the reactivity of the potassium fluoride. In the first case it is presumed to originate from more efficient coordination of the substrate on the potassium fluoride surface, and in the second case a formation of loose ion pairs between the catalyst and fluoride ion is imagined [4, 5]. We believe that this description incompletely represents the nature of processes occurring at the fluorodechlorination in the presence of phase-transfer catalysts.

We selected for the study of fluorodechlorination with potassium fluoride the following compounds: 1,3,5-trifluoro-2,4,6-trichloro- (**Ia**), 1,2,4-trifluoro-3,5,6-trichloro- (**Ib**), and 1,2,3-trifluoro-4,5,6-trichlorobenzenes (**Ic**). Compounds **Ia–c** with similar physical and chemical properties were convenient models for investigation.

The fluorodechlorination of polychlorobenzenes is known to proceed along addition–elimination mechanism with an intermediate formation of an anionic σ -complex [7]. It was presumed that the difference in the fluorination rate of catalytic and non-catalytic reactions could originate not only from the catalyst effect on increasing concentration of the

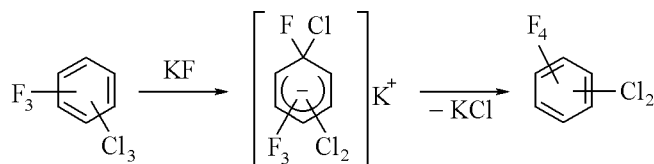


Degree of conversion as a function of reaction time (molar ratio $C_6Cl_2F_4 : KF : \text{catalyst}$ is 1:1:0.05). (1) hexaethylguanidinium chloride (V), (2) tetra(diethylamino)phosphonium bromide (IV), (3) crown ether (18-crown-6) (III), (4) tetraglyme (II), (5) sulfolane (weight ratio $C_6Cl_3F_3 : \text{sulfolane}$ is 1:1).

fluoride ion, but also from stabilization of the corresponding σ -complex. Therewith if the catalyst role in the accelerating the fluorodechlorination is limited to increasing the running concentration of the "active" fluoride ion, the catalytic effect would weakly depend on the substrate nature. On the contrary, if the catalyst takes part in stabilization of the intermediate σ -complex it can be expected that here the fluorodechlorination of the more active substrates would be accelerated more than that of the less active substrates.

On the figure are presented results of fluorodechlorination performed with no catalyst in sulfolane and with no solvent with catalysts: tetraglyme (**II**), 18-crown-6 (**III**), tetra(diethylamino)phosphonium bromide (**IV**), and hexaethylguanidinium chloride (**V**). As seen from the figure, the maximal conversion rate (with respect to the sum of isomers) for trifluorotrichlorobenzenes is observed with compounds **IV** or **V** as catalysts, and the reaction in sulfolane without catalyst is the least efficient.

The analysis of variation in trifluorotrichlorobenzenes **Ia-c** isomeric composition in the course of fluorodechlorination revealed (Table 1), that in all cases the reactivity decreased in the series **Ib**, **Ic**, **Ia**. These data are consistent with the published facts on the effect of fluorine and chlorine atoms on the stability of the anionic σ -complex [7-10].



Ia-c

I, 1,3,5- F_3 (**a**), 1,2,4- F_3 (**b**), 1,2,3- F_3 (**c**).

We analyzed further the rate of variation of the isomeric composition of compounds **Ia-c** as a function of the catalyst nature at the same conversion degree (with respect to the sum of isomers).

As was already stated, when the catalyst does not take part in the σ -complex stabilization, the isomer ratio in trifluorotrichlorobenzenes at the same conversion degree in reactions fluorodechlorination with and without catalyst should be approximately equal. Results of reactions with catalysts **II** and **III** are consistent with this assumption. Isomeric composition of trifluorotrichlorobenzenes forming at the use of these catalysts and without catalyst in sulfolane at the same conversion is approximately the same (Table 1), and in its turn is close to that observed at fluorination of trifluorotrichlorobenzenes with potassium

fluoride with no solvent or catalyst at 350°C. Thus when as catalysts are applied tetraglyme or 18-crown-6 the efficiency of catalysis is not sensitive to the nature of substrate. This result is in agreement with conclusions made in studies of fluorodechlorination of the other substrates in the presence of crown ethers [11].

The pattern observed with the "onium" catalysts, as hexaethylguanidinium chloride and tetra(diethylamino)phosphonium bromide. The difference in isomeric composition as compared to uncatalyzed reaction is already notable at conversion of ~8.5%, and at conversion 20% it is considerable (Table 1). Thus the catalytic effect of catalysts **IV** and **V** significantly depends on substrate, and the most is accelerated the fluorodechlorination of substrate **Ib**, less that of **Ic**, and the least that of **Ia**.

The observed difference in catalytic effect of polyethers **II**, **III**, and "onium" catalysts **IV**, **V** presumably originates from the dissimilar mechanism of their action. The catalytic effect at the use of polyethers **II** and **III** may be rationalized as increase in the concentration of an "active" fluoride ion resulting in acceleration of the fluorodechlorination, irrespective of the place where meet the "active" fluoride ion and the substrate, be it on the solid surface or in the ω -phase. When catalysts **IV** and **V** are applied the catalysis has another character and not only produces higher concentration of the "active" fluoride ions, but is also due to significant participation of these catalysts in the stabilization of the corresponding σ -complexes thus reducing the activation energy of fluorodechlorination.

This conclusion is additionally supported by our data on reaction between tetrafluorodichlorobenzene and potassium chloride (Table 2). This is chlorodefluorination reaction, a process reversed with respect to fluorodechlorination of trifluorotrichlorobenzenes. The data in Table 2 show that the substitution of fluorine by chlorine at the use of catalysts **IV** and **V** under similar conditions occurs in ~30 h to ~17 and 30% respectively, whereas with the crown ether even in 150 h only 1.5% of the initial compound undergoes chlorodefluorination, and in the absence of any catalyst no visible amount of the reaction product forms even in 150 h.

We believe that the reversibility of fluorodechlorination in the presence of catalysts **IV** and **V** additionally evidences that the catalyst play significant role in stabilization of the intermediate σ -complex thus reducing the activation energy of both direct and reverse reactions. The crown ether weakly

Table 1. Fluorodechlorination of trifluorotrchlorobenzenes with potassium fluoride (molar ratio $C_6Cl_3F_3$:KF:catalyst 1:1:0.05, 160°C)

Catalyst	Molar ratio of isomers ^a of $C_6Cl_3F_3$ Ia : Ib : Ic at conversion, %				
	8.5	15	20	25	30
V	1:1.04:0.41	1:0.82:0.36	1:0.68:0.33	1:0.55:0.31	1:0.47:0.29
IV	1:0.93:0.36	1:0.70:0.31	1:0.56:0.28	1:0.44:0.25	1:0.34:0.23
III	1:1.19:0.44	1:1.02:0.43	1:0.92:0.41	1:0.80:0.40	
II	1:1.19:0.45	1:1.19:0.45	1:1.20:0.43		
-	1:1.34:0.43 ^b	1:1.30:0.40 ^b	1:1.29:0.38 ^b		
-			1:1.30:0.49 ^c		

^aInitial molar ratio of isomers (Ia):(Ib):(Ic) 1:1.41:0.48. ^bIn sulfolane. ^cUnder pressure at 350°C.

Table 2. Chlorodefluorination of tetrafluorodichlorobenzene with potassium chloride (molar ratio $C_6Cl_2F_4$:KCl 1:1, 160°C)

Catalyst (mol)	Yield of $C_6Cl_3F_3$, %		
	8 h	16 h	30 h
IV (0.25)	4.0	9.0	17.0
IV (0.05)	2.3	5.3	7.0
V (0.25)	15.0	22.0	32.0
V (0.05)	7.5	11.2	16.5
III (0.05) ^a	-	-	-

^a150 h, yield of $C_6Cl_3F_3$ ~1.5%.

influences the stabilization of the σ -complex, it only increases the concentration of the "active" fluoride ion, and presumably slightly affects the concentration of the chloride ion.

Thus the experimental data obtained evidence that accelerated fluorodechlorination in the presence of "onium" catalysts **IV**, **V** is caused not only by increased concentration of the "active" fluoride ions but also by reduced activation energy of fluorination presumably due to efficient stabilization of the intermediate σ -complex. The higher fluorodechlorination rate in the presence of polyethers **II**, **III** originates mainly from increased running concentration of the "active" fluoride ion.

EXPERIMENTAL

¹⁹F NMR spectra were registered on spectrometer Bruker WP-80 (at 75,398 MHz) in $(CD_3)_2CO$ with hexafluorobenzene as internal reference. Mass spectra were measured on Finnigan Mat ITD-800 instrument,

vaporizer temperature 200°C, ionizing electrons energy 70 eV.

Chromatographic analysis was carried out on a chromatograph Hewlett Packard-5890 equipped with katharometer and a capillary column (30000 × 0.25 mm), stationary phase SE-54, isothermal mode (100°C), carrier gas helium, flow rate 20 ml min⁻¹.

The isomers of dichlorotetrafluorobenzene and trichlorotrifluorobenzene were separated by rectification from the raw product of hexachlorobenzene fluorination. The fractions boiling respectively at 152–153°C and 188–189°C were collected. From the fraction of trichlorotrifluorobenzenes was separated excess isomer **Ia** by freezing at ~0°C in order to have more leveled isomeric composition. The used fractions of $C_6Cl_2F_4$ and $C_6Cl_3F_3$ contained over 99% of the main substance (with respect to isomers sum) according to GLC data. Potassium fluoride dried by spraying (commercial product of the Pilot Plant of the Perm Division of the Federal State Unitary Enterprise "Russian Scientific Center Applied Chemistry") was used without additional purification. Tetraglyme, 18-crown-6, sulfolane of "pure" grade were used without additional purification. Tetra(diethylamino)phosphonium bromide and hexaethylguanidinium chloride (commercial product of the Pilot Plant of the Perm' Division of the Federal State Unitary Enterprise "Russian Scientific Center Applied Chemistry") were recrystallized from benzene.

Fluorodechlorination of polyfluorochlorobenzenes. Specified quantities of $C_6Cl_3F_4$ or $C_6Cl_2F_4$, KF or KCl, and a catalyst were heated at stirring to the required temperature, and sampling was performed intermittently. The samples were analyzed by GLC to determine the conversion degree, and ¹⁹F NMR

spectra were recorded for evaluation of the isomeric composition.

^{19}F NMR spectra of all compounds were consistent with the published data [12]. In the mass spectra of all the initial compounds and the reaction products were present the corresponding molecular ion peaks.

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