Synergism in catalytic halogen-exchange fluorination of 4-chloronitro- and dichlorotetrafluorobenzenes

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Synergism was studied in catalytic halogen-exchange fluorination of 4-chloronitro- and dichlorotetrafluorobenzenes. The synergistic effect in the fluorination of chloroaromatic compounds with potassium fluoride was mainly attributed to separation of the activation functions of catalysts with respect to substrate molecules.

Key words: fluorodechlorination, halogen-exchange fluorination, potassium fluoride, dichlorotetrafluorobenzene, chloronitrobenzene, phase-transfer catalysis, synergism.

Industrially, fluoroaromatic compounds are mainly produced by fluorodechlorination of chloroaromatic compounds with alkali metal (especially potassium) fluorides.¹ Successful fluorodechlorination of chloroaromatic compounds with potassium fluoride (noncatalytic process) depends on, at least, two key factors: (1) the state of the crystal structure of potassium fluoride (primarily, its texture), which is obviously associated with the concentration of "active" potassium fluoride, and (2) the inherent reactivity of a substrate.²⁻⁴ Recently, this process has been significantly intensified by using phase-transfer catalysts.^{5–7} In this case, the reaction conditions are milder, and no solvent is required. A great number of structurally different compounds belonging to various classes were studied as catalysts of fluorodechlorination.^{8–10} Guanidinium derivatives, quaternary phosphonium salts, ammonium salts, cryptates, crown ethers, and polyethers are usually most efficient catalysts for these processes.^{9,10}

The effect of phase-transfer catalysts on fluorodechlorination of aromatic compounds was mainly attributed to the enhanced reactivity of alkali metal fluoride due to either the formation of loose ion pairs⁵ or more efficient coordination of a substrate at the potassium fluoride surface.⁴

According to our investigations,¹⁰ fluorodechlorination of trichlorotrifluorobenzenes with potassium fluoride in the absence of solvents can be catalyzed not only through an increase in the concentration of active potassium fluoride, but also by involving a catalyst in stabilization of an intermediate σ -complex (Scheme 1); in the latter case, the catalytic effect is usually significantly greater.

In a particular situation, either of these effects can dominate, depending on the catalyst nature. Fluorodechlorination of haloarenes with potassium fluoride in Scheme 1



the presence of onium catalysts such as hexaethylguanidinium chloride (1) or tetrakis(diethylamino)phosphonium bromide $(Et_2N)_4PBr$ (2) accelerates mainly because of better stabilization of an intermediate σ -complex (Meisenheimer complex), while acceleration of this reaction with polyethers (18-crown-6 (3) or tetraethylene glycol dimethyl ether (tetraglyme) (4)) predominantly results from an increase in the running concentration of active potassium fluoride.¹⁰ We believe that this increase is not directly attributable to better solubility of active potassium fluoride in the organic phase; most probably, it is due to fatal destruction of the crystal structure of the fluoride surface to give active centers (primarily, as loose ion pairs).

Classification of catalysts according to the activation mechanism in arene fluorodechlorination is fairly conventional and, first of all, indicates domination of one or another mechanism through which a particular catalyst is involved in halogen exchange in an aromatic molecule.

Taking into account that catalysts can accelerate fluorodechlorination of chloroaromatic substrates at different steps of the process—on the one hand, by increas-

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ing the concentration of active potassium fluoride, on the other hand, by lowering the activation energy of the reaction through stabilization of an intermediate σ -complex—synergism (*i.e.*, nonadditive enhancement of the catalytic activity) should be expected for a combination of different catalysts (differing in nature and properties).

Synergistic effects in catalysis are known to arise not only from the formation of new active centers (intermediates), but also from separation of the activation functions of catalysts with respect to substrate molecules in time and space, *i.e.*, for kinetic (dynamic) reasons. Because of this, synergism is a result of the functional organization of the whole catalytic system.¹¹

Results and Discussion

The reactions of a mixture of isomeric dichlorotetrafluorobenzenes and 4-chloronitrobenzene with KF were studied in the presence of catalytic amounts of hexaethylguanidinium chloride, $(Et_2N)_4PBr$ (which efficiently stabilize a σ -complex¹⁰), 18-crown-6, tetraethylene glycol and diethylene glycol dimethyl ethers (which effectively activate potassium fluoride^{10,12}), and their mixtures (see Tables 1, 2).

Fluorodechlorination of dichlorotetrafluorobenzene with KF in the presence of catalytic amounts of diglyme 5, tetraglyme 4, or crown ether 3 under the chosen conditions was found to be very slow (after 6 h, only trace amounts of chloropentafluorobenzene were detected). The fluorination efficiency in the presence of hexaethylguanidinium chloride 1 over 6 h was ~10 or ~20%, depending on the mole fraction of the catalyst (2.5 or 5 mol % of the substrate, respectively) (Table 1). As expected, the catalytic system became substantially more active when hexaethylguanidinium chloride is combined with polyethers. The synergistic effect was greater for the lower mole fraction of catalyst 1 (2.5 mol %). In this case (for an equimolar ratio of hexaethylguanidinium chloride 1 to a polyether), the conversion of dichlorotetrafluorobenzene was virtually doubled (see Table 1, entries 1, 9, 12, 14). When the content of catalyst 1 was 5 mol %, the maximum synergistic effect results in the increase in the yield of fluorination products at best by ~7%; *i.e.*, the conversion gain was only $\sim 35\%$ (see Table 1, entries 2, 7). The reduced synergistic effect at the higher concentration of hexaethylguanidinium chloride 1 is probably due to the fact that this catalyst not only stabilizes a σ -complex but also efficiently increases the concentration of active potassium fluoride, thus reducing the demand in a polyether for activation of potassium fluoride. It was noted that the polyethers studied contribute differently to the acceleration of fluorodechlorination of dichlorotetrafluorobenzene. A combination of hexaethylguanidinium chloride 1 with tetraglyme 4 was most efficient, all other factors being equal (the mole fractions of catalyst 1 and a polyether were 5 mol %); for its combination with 18-crown-6 3, the effect was smaller; the poorest results were obtained for a system containing diglyme 5 (see Table 1, entries 7, 5, 4). When the mole fractions of hexaethylguanidinium chloride and polyethers are 2.5 mol %, the efficiency order is somewhat different: $4 \approx 5 > 3$ (see Table 1, entries 12, 14, 9). A variation in the efficiency of the polyethers with the concentration of catalyst 1 can be due either to their competitive ion-dipole interactions with hexaethylguanidinium or potassium cations or to diffusion (instead of kinetic) control of the process at increased concentrations of catalyst 1. Apparently, the same reasons are responsible for insignificant changes in the conversion of dichlorotetrafluorobenzene when the mole fractions of catalysts 1 and 5 are increased from 2.5 to 5 mol % (see Table 1, entries 14, 4).

Close results were obtained in the study of fluorodechlorination of 4-chloronitrobenzene (Table 2). The conversion of 4-chloronitrobenzene in the presence of tetraglyme **4** alone (0.025 mol) did not exceed 2.5% over 5 h. Synergism arose in a catalytic system of $(Et_2N)_4PBr 2$ and tetraglyme **4** (see Table 2). With an increase in the tetraglyme concentration, the synergistic effect monotonically grew throughout the range studied to a maximum value at a $(Et_2N)_4PBr$: tetraglyme ratio of 1:8.

In fluorination of 4-chloronitrobenzene with potassium fluoride in the presence of equal concentrations of $(Et_2N)_4PBr\ 2$ and tetraglyme 4, the synergistic effect is slightly weaker than that obtained in the fluorination of $C_6F_4Cl_2$ in the presence of hexaethylguanidinium chloride 1 and tetraglyme 4 (see Table 1, entry 12; Table 2, entry 3). This can be due to different reactivities of the substrates¹³ and different efficiencies of onium catalysts (*i.e.*, the ability of stabilize a σ -complex)¹⁰ (Scheme 2).

Scheme 2



 $R^2 = F, n = 4, R^1 = Cl$

Similar synergistic effects in exchange fluorodechlorination in the presence of two different catalysts were noted while studying reactions of other substrates and catalysts.

1 Entry 1 0.06 0.55 98.96 0.43 Entry 2 0.07 5.41 93.60	2 . Catalyst 0.07 2.47 96.70 0.75 . Catalyst 0.1	3 1 (6.58 g 0.07 4.54 94.52 0.87 1 (13.16	4 g (0.025 n 0.08 6.30 92.75 0.87	5 nol)) 0.09 7.57 91.3 1.05	6 0.09 8.67					
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Entry 2 0.07 5.41	Catalyst 0.1	1 (13.16	·	1.03	1.13					
0.07 5.41	0.1	Entry 2. Catalyst 1 (13.16 g (0.05 mol))								
5.41		0.11	0.14	0.16	0.18					
03 60	10.62	13.0	15.41	17.15	18.48					
22.07	88.12	85.62	83.18	81.39	79.91					
0.83	1.16	1.27	1.27	1.3	1.43					
Entry 3. Catalysts 1 (13.16 g (0.05 mol)										
	+5(1.3)	4 g (0.01	mol))							
0.08	0.09	0.11	0.13	0.15	0.18					
7.53	11.74	14.07	16.24	17.46	19.25					
91.50	87.10	84.55	82.34	80.90	79.05					
0.89	1.07	1.27	1.29	1.49	1.52					
Entry 4. Catalysts 1 (13.16 g (0.05 mol))										
	+ 5 (6.7	g (0.05 r	nol))							
0.07	0.08	0.13	0.14	0.16	0.20					
6.66	10.82	14.03	15.34	17.07	18.76					
92.50	88.01	84.56	83.28	81.45	79.65					
0.76	1.09	1.29	1.24	1.32	1.39					
Entry 5. Catalysts 1 (13.16 g (0.05 mol))										
	+ 3 (13.2	2 g (0.05	mol))							
0.06	0.10	0.11	0.14	0.18	0.19					
5.94	11.74	14.85	17.58	18.87	20.88					
93.06	86.89	83.69	80.99	79.65	77.63					
0.94	1.27	1.35	1.29	1.30	1.30					
Entry 6. Catalysts 1 (13.16 g (0.05 mol))										
+ 4 (5.56 g (0.025 mol))										
0.05	0.10	0.10	0.13	0.15	0.17					
7.41	12.96	15.52	18.06	19.72	20.99					
91.35	85.53	82.76	80.19	78.49	77.11					
1.19	1.42	1.65	1.62	1.64	1.73					
Entry 7	Catalyst	s 1 (13.16	g (0.05 r	nol))						
, <i>'</i> ,	+ 4 (11.1	2 g (0.05	mol))	//						
0.08	0.17	0.19	0.23	0.30	0.33					
9.6	16.01	19.44	20.00	24.53	25.82					
89.33	83,11	79.66	78.72	73.83	73.16					
0.98	0.71	0.71	1.05	1.34	0.69					
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Table 1. Effects of the nature of the catalyst and the reaction time on the percentage of the products in the fluorodechlorination of dichlorotetrafluorobenzene (219 g, 1 mol) with potassium fluoride (58 g, 1 mol)

Note. Chlorodefluorination of $C_6F_4Cl_2$ yielded $C_6F_3Cl_3$.¹⁰

For example, a combination of tetraphenylphosphonium bromide or chloride with 18-crown-6 or polyethylene glycol dimethyl ethers is more active in fluorodechlorination of chlorobenzaldehydes than the phenylphosphonium salt alone.^{14,15}

Com-	Reaction time/h							
pound	1	2	3	4	5	6		
	Entry 8. Catalysts 1 (6.58 g (0.025 mol))							
	+ 3 (3.3 g (0.0125 mol))							
C ₆ F ₆	0.07	0.07	0.08	0.09	0.10	0.11		
C ₆ F ₅ Cl	1.60	3.84	6.16	8.35	9.76	11.08		
$C_6F_4Cl_2$	97.83	95.14	92.84	90.59	89.13	87.82		
$C_6F_3Cl_3$	0.51	0.97	0.92	0.97	1.01	0.99		
	Entry 9. Catalysts 1 (6.58 g (0.025 mol))							
		+ 3 (6.6	g (0.025	mol))				
C_6F_6	0.05	0.05	0.06	0.09	0.08	0.09		
C_6F_5Cl	2.25	4.66	8.47	10.62	12.61	13.90		
$C_6F_4Cl_2$	97.07	94.53	90.59	88.46	86.47	85.11		
$C_6F_3Cl_3$	0.63	0.76	0.88	0.83	0.84	0.90		
Entry 10. Catalysts 1 (6.58 g (0.025 mol))								
	+ 3 (13.2 g (0.05 mol))							
C_6F_6	0.06	0.07	0.09	0.10	0.13	0.16		
C_6F_5Cl	7.10	11.08	14.21	16.46	18.16	19.92		
$C_6F_4Cl_2$	92.40	87.73	84.60	82.37	80.66	78.63		
$C_6F_3Cl_3$	0.44	1.12	1.10	1.07	1.06	1.29		
Entry 11. Catalysts 1 (6.58 g (0.025 mol))								
	-	+ 4 (2.78	g (0.0125	5 mol))				
C ₆ F ₆	0.06	0.07	0.09	0.11	0.14	0.16		
C_6F_5Cl	7.10	11.08	14.21	16.47	18.17	19.90		
$C_6F_4Cl_2$	92.35	88.29	85.05	82.71	80.89	79.28		
$C_6F_3Cl_3$	0.49	0.56	0.65	0.71	0.82	0.66		
Entry 12. Catalysts 1 (6.58 g (0.025 mol)								
+ 4 (5.56 g (0.025 mol))								
C_6F_6	0.06	0.08	0.11	0.14	0.15	0.17		
C ₆ F ₅ Cl	6.96	11.78	15.43	18.05	19.80	21.23		
$C_6F_4Cl_2$	92.43	87.48	83.78	81.27	79.41	77.89		
$C_6F_3Cl_3$	0.55	0.60	0.69	0.55	0.64	0.71		
Entry 13. Catalysts 1 (6.58 g (0.025 mol))								
+ 4 (11.12 g (0.05 mol))								
C _c E _c	0.05	0.09	0.12	0.12	0.12	0.14		
C ₆ F ₆ Cl	6.15	10.12	13.46	15.64	17.28	18.98		
C ₄ E ₄ Cl ₂	93.08	88.91	85.46	83.17	81.64	79.92		
$C_6F_3Cl_3$	0.71	0.89	0.96	1.07	0.96	0.96		
Entry 14 Catalysts 1 (6.59 \times (0.025 mol))								
	Litty 17	+ 5 (3.32	2 g (0.025	mol))				
CcEc	0.06	0.07	0.12	0.15	0 14	0.16		
$C_{c}F_{c}C^{1}$	8.34	12.01	17.64	19.40	19.80	21.55		
$C_6F_4Cl_2$	91.60	87.32	81.84	80.25	79.54	77.82		
$C_6F_3Cl_2$	_	0.60	0.40	0.20	0.52	0.47		

Apparently, here the synergism in catalytic fluorodechlorination is also associated with separation of the activation functions of catalysts with respect to substrate molecules (the onium catalyst, namely, tetraphenylphosphonium halide, activates an aro-

Table 2. Effects of the nature of the catalyst and the reaction time on the percentage of the products in the fluorodechlorination of 4-chloronitrobenzene (157.56 g, 1 mol) with potassium fluoride (58 g, 1 mol)

Com-	Reaction time/h						
pound	0.5	1	2	3	4	5	
Entry 1. Catalyst 2 (9.98 g (0.025 mol))							
$C_6H_4FNO_2$ $C_6H_4CINO_2$	3.66 96.34	6.53 93.46	9.55 90.46	10.26 89.74	10.40 89.56	10.22 89.78	
Entry 2. Catalysts 2 (9.98 g (0.025 mol)) + 4 (2.78 g (0.0125 mol))							
C ₆ H ₄ FNO ₂ C ₆ H ₄ CINO ₂	6.97 92.77	11.35 88.65	12.09 87.90	13.43 86.57	15.23 84.77	17.25 83.75	
Entry 3. Catalysts 2 (9.98 g (0.025 mol)) + 4 (5.56 g (0.025 mol))							
C ₆ H ₄ FNO ₂ C ₆ H ₄ CINO ₂	5.28 94.72	8.78 91.21	15.28 84.72	15.54 84.46	15.64 84.34	18.08 81.90	
Entry 4. Catalysts 2 (9.98 g (0.025 mol)) + 4 (11.12 g (0.05 mol))							
C ₆ H ₄ FNO ₂ C ₆ H ₄ CINO ₂	7.34 92.70	13.78 86.22	16.03 83.97	18.47 81.53	18.79 81.21	18.33 81.67	
Entry 5. Catalysts 2 (9.98 g (0.025 mol)) + 4 (44.48 g (0.2 mol))							
C ₆ H ₄ FNO ₂ C ₆ H ₄ ClNO ₂	9.13 90.87	14.42 85.58	20.23 79.77	25.91 74.09	27.79 72.21	29.70 70.30	

matic molecule, while a polyether activates potassium fluoride).

This agrees with data obtained in the study of the catalytic activity of tetraphenylphosphonium bromide.⁶ The replacement rate for chlorine in chloronitropyridine was determined in different aprotic solvents in the presence and absence of tetraphenylphosphonium bromide. It was concluded from the resulting dependence⁶ that Ph_4PBr not only increases the concentration of fluoride ions in the organic phase, but also helps the solvent to stabilize an intermediate Meisenheimer complex. At the same time, other researchers¹² who have studied the catalytic activity of crown ethers in fluorodechlorination reactions believe that replacement of a chlorine atom by fluorine accelerates mainly because of higher nucleophilicity of potassium fluoride.

A similar synergistic effect was also observed in fluorodechlorination of hexachlorobenzene with potassium fluoride supported on calcium (or barium) fluoride in the presence of $(Et_2N)_4PBr.^{16}$ In this case, the concentration of active KF probably increases because of its support on CaF₂ or BaF₂, while $(Et_2N)_4PBr$ activates the aromatic substrate.

The experimental results presented here, as well as the published literature data,^{17,18} fit well the proposed mechanism for synergism in the catalytic fluorodechlorination

of chloroarenes with potassium fluoride. As shown earlier,^{6,10,12} the use of catalysts in fluorodechlorination of chloroarenes either increases the concentration of active potassium fluoride or enhances the reactivity of a substrate (by means of stabilization of an intermediate σ -complex), while a combination of catalysts with different mechanisms of involvement in fluorodechlorination results in the observed synergism (i.e., nonadditive increase in the activity of the whole catalytic system). An alternative version, where the catalytic activity increases because of the mutual influence of catalysts (e.g., as a result of specific solvation of an onium salt in a polyether, which can change the anion transfer activity), seems to be unlikely. In such a case, synergism arising in the fluorination of hexachlorobenzene¹⁶ from a combination of an onium catalyst and potassium fluoride supported on an inert carrier (CaF₂, BaF₂) finds no explanation. Certainly, fine details of the mechanism of synergism in catalytic halogen-exchange fluorination in a liquid-solid system remain unclear so far and further, including kinetic, investigations are required.

Experimental

¹⁹F NMR spectra were recorded on a Bruker WP-80 instrument (75.398 MHz) in deuteroacetone with hexafluorobenzene as the internal standard. The course of the reaction was monitored by chromatography using a Hewlett Packard 5890 chromatograph (katharometer as a detector, capillary column 30 m × 0.25 mm, SE-54 phase, isothermal regime (100 °C), helium as a carrier gas (20 mL min⁻¹). Mass spectra were recorded on a Finnigan Mat ITD-800 instrument (ionization chamber temperature 200 °C, ionizing voltage 70 eV).

Materials. Potassium fluoride, diethylene glycol and tetraethylene glycol dimethyl ethers, 18-crown-6, 4-chloronitrobenzene (high-purity grade), $(Et_2N)_4PBr$, and hexaethylguanidinium chloride were conditioned according to the known procedure.¹⁰ Dichlorotetrafluorobenzene was isolated by fractional distillation (fraction with b.p. 152–153 °C) from a product obtained in the catalytic fluorodechlorination of hexachlorobenzene. The dichlorotetrafluorobenzene obtained was a mixture of isomeric 1,3-dichloro-2,4,5,6-tetrafluorobenzene (94.5%), 1,2-dichloro-3,4,5,6-tetrafluorobenzene (5%), and 1,4-dichloro-2,3,5,6-tetrafluorobenzene (0.5%).

Fluorodechlorination of chlorobenzenes. Given amounts of $C_6Cl_2F_4$ or 4-Cl- $C_6H_4NO_2$, KF, and a catalyst (or a mixture of catalysts) were heated with stirring at 140 °C. The reaction mixture was periodically sampled and analyzed by GLC for conversion degree.

The ¹⁹F NMR spectra of all starting reagents and reaction products were identical with the literature data.¹⁹ Their mass spectra contained the corresponding molecular ions.

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