# Heterogeneous fluorination of chlorine containing polymers with 18-crown-6 as phase transfer agent

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Effectiveness of alkali metal fluorides, complexed with crown ethers, as fluorinating agents, was investigated in nitrobenzene as mediating solvent. Partial fluorination of the surface of the crosslinked film of chlorinated polyethylene occurs within the first 2 h at 80°C. Further reaction leads to dehydrochlorination only. Up to 50% of chlorine in polyepichlorhydrin (Herchlor-H) may be replaced by fluorine. Further reaction is strongly inhibited by the presence of fluorine substituents in the neighbourhood of unsubstituted chlorines. 'Plateau' is reached after about 10 h at 140°C. In all investigated systems elimination, $E$, competes with substitution, $S$. It was suggested that the same transition state complex may be responsible for the two reactions. The energy of activation of the two processes is $\sim 5$ kcal mol$^{-1}$. The $S/E$ ratio decreases in the following order: primary > secondary >>> vicinal.

**(Keywords: fluorination; crown complexes; chlorinated polyethylenes; polyepichlorhydrin; phase transfer)**

## INTRODUCTION

Heterogeneous modification of polymers gained much attention in recent years[1-4]. Reactions leading to such modifications may often be facilitated by the 'onium' type phase transfer agents[5,6] as well as by cyclic[3,7,8] and acyclic polyethers[3,8]. Hoffman reported more than thirty years ago[9] that potassium fluoride dissolved in ethylene glycol acted as an effective fluorinating agent. Liotta *et al.*[10] suggested more recently that fluorine becomes particularly reactive when its salt is dissolved in an aprotic solvent as a result of interaction of the cation with a 'crown' ether. Though the concept of 'naked' anions suggested by these authors is rather controversial, (^{19}F-n.m.r. studies of the KF-crown solutions show[11] that fluorine anion is closely associated with the complexed counter ion even in such solvents as $CH_3CN$ and nitrobenzene), there seems to be no doubt that anions may be activated by interaction of their counter-ions with 'crown' ethers and the use of KF in conjunction with 'crown' ethers seems to be advantageous for some fluorination reactions[10,12,13].

It was decided, therefore, to explore the possibility of using this approach for the substitution of chlorine by fluorine in certain chlorine containing polymers. Such reactions involve two or three phases when polymers are soluble or insoluble, repsectively, in the mediating solvent. Reactions on polymers were compared with those of their low molecular weight analogues. Results of these studies are discussed in this paper.

## EXPERIMENTAL

### Chlorine containing polymers

Three types of $\sim 20$ $\mu$m thick polyethylene films were used for the preparation of chlorinated polyethylenes: LDP—Blow extruded, low density polyethylene, Ipethene 6000, $d = 0.916$ g cm$^{-3}$, $\alpha_c = 24\%$, Petrochemical Industries (Israel); RCP—Biaxially oriented, radiation crosslinked polyethylene, $\alpha_c = 24\%$; Cryovac D-925, Grace Corp. (Canada); and HDP—Blow extruded, high density polyethylene, m.p. 128°C, $\alpha_c = 39.8\%$. The polyethylene films were chlorinated at room temperature by $Cl_2$ gas in presence of actinic light. A low intensity fluorescence lamp and a high intensity u.v. lamp (Hanau Type 002314) have been used for the chlorination of LDP and HDP and of RCP, respectively. The chorine content of thus prepared CLDP and CHDP films is 56.1% and 33.5%, respectively. (This corresponds[14] to $\sim 74\%$ Cl in the amorphous phase of CLDP and $\sim 56\%$ Cl in the amorphous phase of CHPD). The chlorination of RCP was largely restricted to its surface because of its intensive illumination during the reaction[14]. The overall chlorine content of thus prepared CRCP films is 8.8% Cl but its content in the 0.5 $\mu$m thick surface layer was estimated by ATR-*FT*i.r. spectroscopy to be $\sim 45\%$.

PVC powder, 56.6% Cl, Plastisol grade, Rhodopas XHP, Rhone-Poulenc (France) was used as supplied. CPVC was prepared from PVC by suspending it in $CCl_4$ saturated with $Cl_2$ and illuminating with actinic light. % Cl of thus prepared CPVC is 61.8%.

Polyepichlorhydrin (PECH), 38.2% Cl, Herchlor H, Hercules Inc. (USA) was used as supplied.

*Model compounds*

2-Chlorooctane, Eastman-Kodak, practical; 1-chloro-octane; 1,1,2,2-tetrachloroethane; 1,1,2,2-tetrachloro-ethylene; *t*-butyl chloride; and bis(chloro ethyl)ether; all Fluka, purum. Perchlorinated polyethylene glycol was prepared from PEG-1000, Sigma, $MW \sim 1000$ by dissolving it in $CCl_4$ and chlorinating in presence of actinic light at *RT*. Precipitate obtained after 10 h of chlorination was filtered off, washed with methanol and dried *in vacuo*. Chlorine content of CPEG is 76.7% ($\%Cl_{calc} = 77.7$) and % H < 0.2%. 1,2-Dichloro-2-methylpropane was prepared from *t*-butyl chloride by controlled chlorination in $CCl_4$. Reaction mixture, from which $CCl_4$ was distilled off when conversion reached $\sim 20\%$ was used without any further purification.

*Solvent and reagents*

Nitrobenzene (NB), BDH, >99% by g.l.c. was dried overnight on Molecular Sieves 4A and distilled *in vacuo*; KF and NaF, Merck, puriss, were dried overnight *in vacuo* at 100°C. Pentaoxycyclopentadecane (15-0-5), Aldrich, practical and hexaoxycyclooctadecane (18-0-6), 98% purity by g.c. (Borregaard, Norway), were used without purification. The two isomers of the dicyclohexyl-18-0-6 (DCC) were isolated from the commercial product, Aldrich, technical, as described elsewhere[15].

*Fluorination of the samples*

Samples were introduced into reaction flasks equipped with magnetic stirrers and reflux condensers. Solution of a crown ether in NB and an excess of dry fluoride was added. The reaction mixtures were kept under a blanket of dry argon, stirred, and the desired temperatures were maintained for various time intervals.

*Analytical procedures*

G.c. analysis of the reaction mixtures was performed on a Tracor 560 Chromatograph with FI detector using a $\frac{1}{4}'' \times 6\frac{1}{2}'$ glass column with 15% QF-1 and 10% DC 200 on Chromosorb Q (60–80 mesh). Finnigan 1015 Mass spectrometer coupled with a gas chromatograph was used for peak identification.

N.m.r. spectra of the samples were recorded at 270 MHz on a Bruker WH-270 Spectrometer.

*Determination of Cl and F*

Polymer samples were washed with ether and water and dried to a constant weight *in vacuo*. (For PECH, soluble in NB, solvent was first evaporated and the residue was washed with water only). %Cl and %F of the dry samples was determined by standard microanalytical procedures[16]. The i.r. spectra were recorded on the Nicolet MX-10 FTIR machine, and surface of the films was probed using the Attenuated Total Reflection (ATR) attachment equipped with a KRS-5 crystal. The depth of penetration, $d_p$, was estimated[17] using the equation:

$$d_p = \lambda/[\sin^2\theta - (n_2/n_1)^2]^{1/2}$$

where $\lambda$, $\theta$, $n_1$ and $n_2$ denote wavelength and angle of the incident radiation and refractive indices of the crystal and sample respectively. %F and %Cl in the surface layers of

the polyethylene films was estimated by comparing the integrated intensities of the $1112\,cm^{-1}$ and the $610\,cm^{-1} + 662\,cm^{-1}$ peaks, respectively, with the integrated intensity of the $720\,cm^{-1}$ band, due to the $CH_2$ rocking mode, which served as an internal standard. Calibration curves relating the respective relative absorbances (expressed by $A_{1112}/A_{720}$ and $[A_{610} + A_{662}]/A_{720}$) with the fluorine and the chlorine content of the samples, are shown in *Figure 1*. They were derived from the i.r. transmission spectra of the films and their Cl and F content determined by microanalysis.

*Solubility measurements*

Magnetically stirred solutions of 18-0-6 and of 15-0-5 in NB were kept under blanket of dry argon and equilibrated at constant temperatures for $\sim 12$ h with an excess of dry salts. Aliquots of the equilibrated solutions were filtered through a $0.5\,\mu m$ Millipore filter using a Millipore pressure syringe. Salts were extracted from the NB solutions using hot deionized water. Aqueous solutions were brought to a constant volume and the concentration of the cations was determined with Varian Techtron 1200 Atomic Absorption Spectrometer. Concentrations of $Cl^-$ and $F^-$ in the aqueous solutions were determined by volumetric titrations[16].

## RESULTS AND DISCUSSION

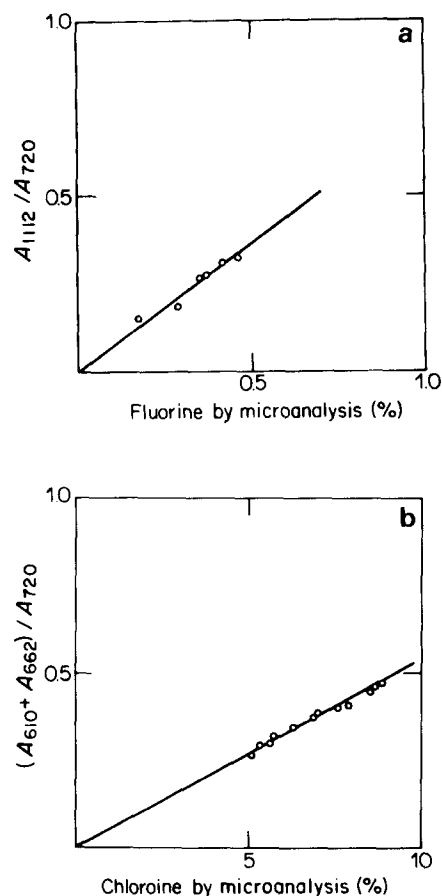Effectiveness of NaF, KF, RbF as fluorinating agents in conjunction with 15-0-5, 18-0-6 and the two isomers of



Figure 1 Calibration curves relating i.r. absorbance with %Cl and %F. (a) Integrated relative i.r. absorbance at 1112.4 cm⁻¹ vs. fluorine content. (b) Integrated relative i.r. absorbance at 660 and 610 cm⁻¹ vs. chlorine content

DCC was checked in benzene, THF, $CH_3CN$, and nitrobenzene as mediating solvents. Nitrobenzene was chosen because of its relatively low solvation power combined with high dielectric constant and high boiling point. Experiments conducted at 60°C with 1-chlorooctane, 2-chlorooctane, and sym-tetrachloroethane as model compounds indicated that only potassium fluoride is reactive under such conditions, while the reactivity of NaF and RbF complexes is very low. The reaction rates seemed to be faster in nitrobenzene than in $CH_3CN$ which was previously used by some investigators as mediating solvents for similar systems[10,12,13]. Such preliminary experiments also indicated that reaction rates were significantly depressed by the presence of trace amounts of water. Accordingly, anhydrous KF in contact with solutions of 18-0-6 in dry nitrobenzene was chosen as fluorinating system for the substitution of chlorine by fluorine in the chlorine containing polymers. The concentrations of the KF (18-0-6) complexes in nitrobenzene, equilibrated at various temperatures, with dry KF are summarized in *Table 1*. As may be seen from the tabulated data, the solubility of KF in nitrobenzene is nearly proportional to the concentration of the 'crown' ether and it increases with the increase in temperature. At 80°C the concentration of KF (18-0-6) complex is 0.5 M solution of the 18-0-6 'crown' in nitrobenzene is $\sim 1.5 \cdot 10^{-2}$ M.

Chlorinated polyethylene films and PVC and CPVC powders were reacted at 80°C. The rate of removal of chlorine from the polymer is shown in *Figure 2*. Reaction rates increase in the order:

$$CRCP < PVC < CHDP < CPVC < CLDP$$

I.r. spectra of the reacted samples as well as their fluorine content reveal, however, that fluorination reaction pro-

**Table 1** Solubility of KF in nitrobenzene in presence of 18—0—6

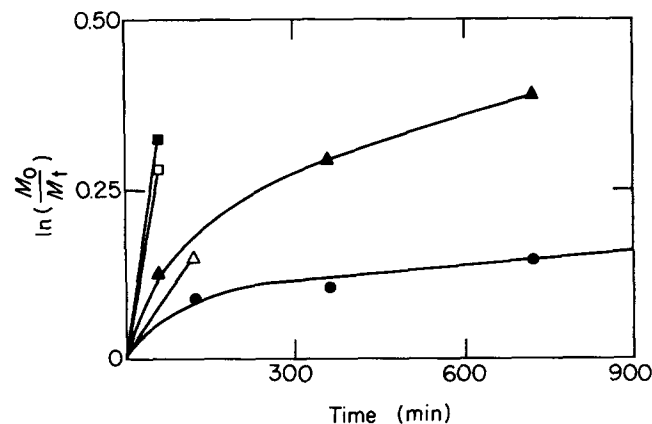| Temperature (°C) | [18—0—6] (M) | | | |
| --- | --- | --- | --- | --- |
| | none | 0.05 | 0.20 | 0.50 |
| | (KF) + (KF, crown) (mM) | | | |
| 60° | 0.23 | 2.7 | 6.7 | — |
| 80° | — | — | ~8 | ~15 |
| 100° | — | — | 8.5 | 21.4 |
| 140° | — | — | 14.5 | — |



**Figure 2** Semi-logarithmic plots of $M_0/M_t$ vs. time for the chlorinated polymers. Temperature 80°C; 0.5 M [18-0-6] in nitrobenzene. (■) CLDP; (▲) CHDP; (●) CRCP; (□) CPVC; (△) PVC
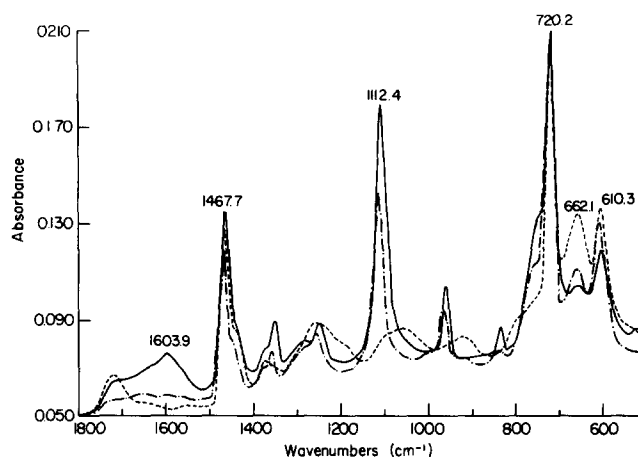


**Figure 3** ATR-*FT*i.r. spectra of the surface of CRCP films. (---) CRCP film; (—·—·—) after 2 h of reaction; (———) after 12 h of reaction
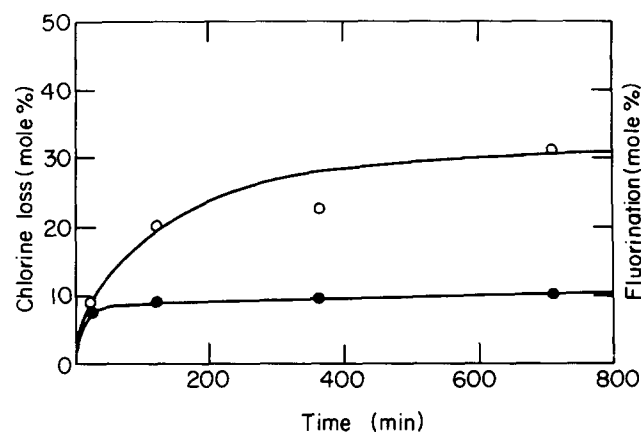


**Figure 4** Modification of the surface of a CRCP film. (○) Total conversion; (●) fluorination

vides a major reaction path for CRCP only. For other investigated materials the dehydrochlorination is predominant (85–95%). ATR-*FT*i.r. spectra of the surface layer ($\sim 0.5$ $\mu$m thick) of a CRCP film and of its reaction products are shown in *Figure 3*. Substitution of chlorine by fluorine in the surface layer may conveniently be followed by the increase in the absorption maximum at $1112$ cm$^{-1}$ (C–F stretching mode). The decrease in the intensity of the 662 and 610 cm$^{-1}$ absorption bands (C–Cl stretching modes) is due to the fluorination and to the dehydrochlorination reaction indicated by the appearance of an absorption maximum at 1604 cm$^{-1}$. Progress of fluorination and of overall modification (substitution + elimination) of the surface of the CRCP film is depicted graphically in *Figure 4*. It is evident that fast fluorination of the surface of CRCP, which takes place at the onset of the reaction, stops when about 10% of chlorine atoms are substituted by fluorines. Further reaction is slower and seems to lead to dehydrochlorination only.

Model compounds with primary, secondary, tertiary, as well as vicinal and geminal chlorine atoms were reacted under analogous conditions in order to understand the reason for such behaviour of the CRCP films. Results of such experiments are summarized in *Table 2*. Inspection of the tabulated data reveals that substitution competes successfully with elimination for the primary and for the perchlorinated chlorides. The relative rates of substi-

**Table 2** Reaction of organic chlorides with KF in nitrobenzene[1]

| $\alpha$-substituent | Substrate[2] | Products | Temp. (°C) | Time (h) | Yield[3] (%) | S/E |
|---|---|---|---|---|---|---|
| Primary | — | $CH_3(CH_2)_5CH_2CH_2Cl$ | $CH_3(CH_2)_5CH_2CH_2F$ $CH_3(CH_2)_5CH=CH_2$ | 100 | 92 | 8.6 | 91/9 |
| | OR | $ClCH_2CH_2OCH_2CH_2Cl$ | $ClCH_2CH_2OCH_2CH_2F$ $ClCH_2CH_2OCH=CH_2$ | 100 | 48 | 33.5 | 70/30 |
| Secondary | — | $CH_3(CH_2)_5CH(Cl)CH_3$ | $CH_3(CH_2)_5CH(F)CH_3$ $CH_3(CH_2)_5CH=CHCH_3$ | 100 | 210 | 6.7 | 63/37 |
| Tertiary | — | $(CH_3)_3CCl$ | none | 80 (reflux) | 66 | none | none |
| Vicinal and Geminal | — | $CHCl_2 \cdot CHCl_2$ | $CH(Cl)=CCl_2$ | 100 | 5 | 37.2 | 0/100 |
| Vicinal | Cl | $CH_2Cl \cdot C(Cl)(CH_3)_2$ | $CHCl=C(CH_3)_2$ | 80 | 3.7 | 6.0 | 0/100 |
| Primary Tertiary Geminal | $Cl_2$ | $CHCl_2 \, C(Cl)(CH_3)_2$ | $CHCl_2 \cdot C(CH_3)=CH_2$ $CHClF \cdot C(Cl)(CH_3)_2$ | 80 | 3.7 | >99 | ~50/50 |
| Other | — | $CCl_2=CCl_2$ | none | 100 | 36 | none | none |
| | — | $+C_2Cl_4O+_n^4$ | $+C_2Cl_{3.6}F_{0.4}O+_n$ | 100 | 48 | 100 | 100/0 |

[1] In presence of 0.5 M 18—0—6
[2] Substrate = 2.5 M
[3] Yield based on g.c. data
[4] Perchlorinated PEG—1000

tution vs. elimination seem to decrease in the following order: primary > secondary; geminal > vicinal. For the isolated tertiary chlorides both elimination and substitution is too slow to be detected. The rates of both reactions decrease in the following order: geminal > vicinal ≫ primary > secondary ≫ tertiary ~ vinyl. The initial fast and selective fluorination of the CRCP films is consistent with the hypothesis that $>C(Cl)_2$ and $-CH(Cl)_2$ groups vicinal to the tertiary chlorine atoms are present in the film surface. The following scheme may account for our experimental findings:
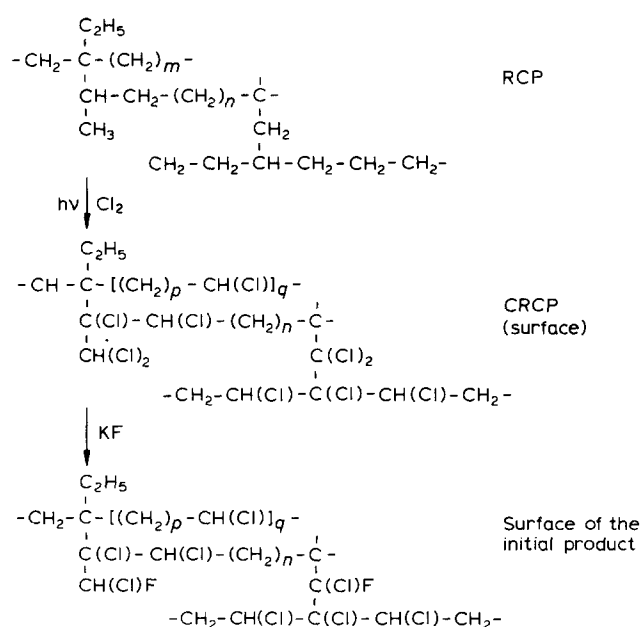


**Figure 5**

The proposed scheme is based on the observation that chlorination of methyls and methylenes is enhanced by C–Cl in $\beta$ position. Hence, the perchlorination of the methylene groups and chlorination of the methyl groups of the low density polyethylene may be facilitated by the tertiary chlorines adjacent to them which will be the first to be formed during the chlorination reaction. Obviously, the number of tertiary carbons is greatly enhanced by the radiation crosslinking of the low density polyethylene.

*Fluorination of poly(epichlorohydrin) (PECH)*

Data shown in column 3 of *Table 2* indicate that the rate of substitution of chlorine by fluorine is greatly enhanced by an etheral group in $\beta$-position to the C–Cl bond. PECH is a commercially available polymer in which such active chlorine atoms are available. The reactivity of such chloromethyl groups is well known and the substitution by amines, phenols, thiophenols and thioamides has recently been investigated[5,18,19].

PECH and its reaction products are soluble in nitrobenzene. A two phase system is, therefore, involved in fluorinations conducted under our experimental conditions. Reaction of PECH with KF (18-0-6) complex in nitrobenzene was investigated at 100°C and 140°C. Typical PMR spectrum of a reaction product is shown in *Figure 6*. Doublet which appears at 4.28 ppm is assigned to the methylene protons in $CH \cdot CH_2F$ and the singlet which appears at 4.50 ppm to the vinyl protons of the $C=CH_2$ group. The respective intensities of these signals reveal that a 70:30 ratio of substitution to elimination is maintained during reactions carried out at 100 as well as at 140°C.

In the presence of an excess of solid KF, the concentration of KF (18-0-6) should remain constant during the entire reaction. One could expect, therefore, that the reaction may be accounted for in terms of pseudo first-

order kinetics. Semilogarithmic plots shown in *Figure 7* reveal, however, that the expected straight lines start to deviate from linearity at higher conversions. These results can be rationalized by assuming a sharp decrease in the rate constant of the reaction at 33% conversion for reaction carried out at 100°C and at 66% conversion for reaction carried out at 140°C, respectively. Data summarized in *Table 3* show that the concentration of fluorine ions in the solution is not depressed by the presence of chloride ion. The sharp decrease in the reaction rate at higher conversions cannot be, therefore, attributed to the decrease in the concentration of the fluorinating species, due to formation of KCl during the reaction. The possibility that the slow-down may be due to a reversed reaction leading to chlorination of the fluorinated groups can also be ruled out, since such reaction does not occur when the product of fluorination is exposed at 140°C to a solution of 18-0-6 in nitrobenzene equilibrated with KCl only. The
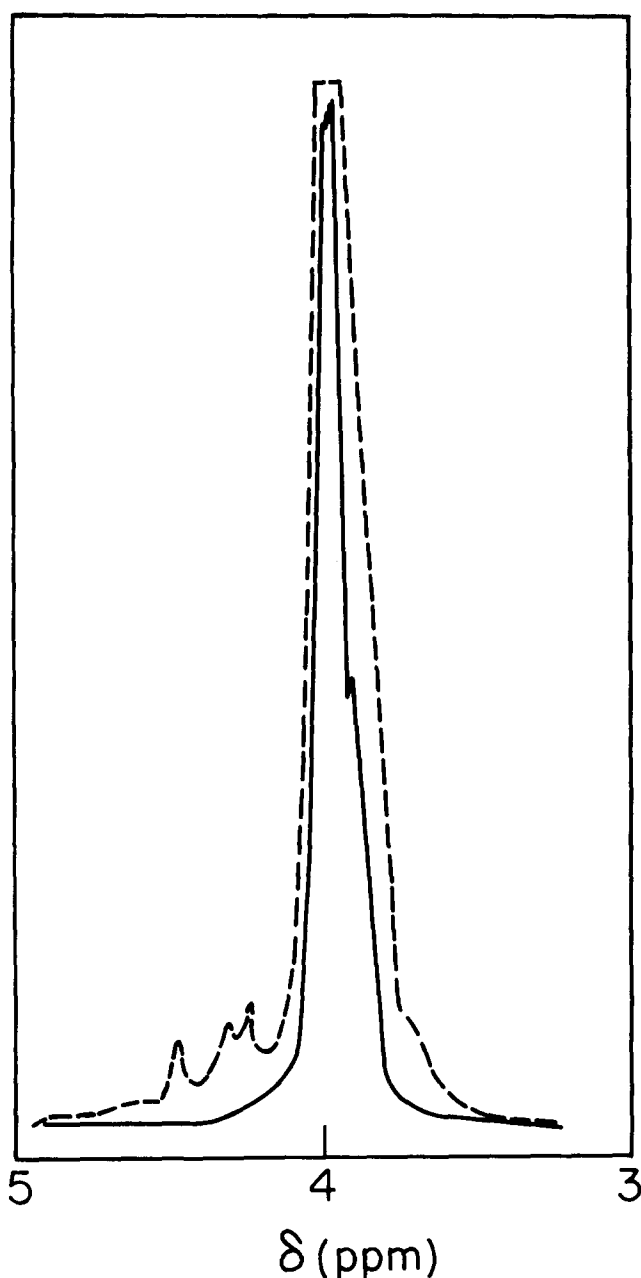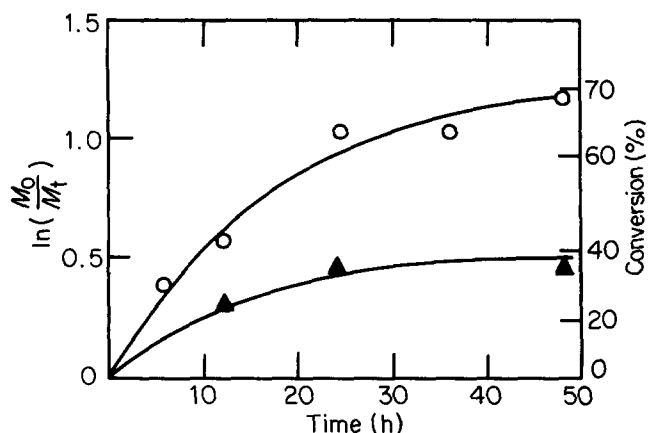


**Figure 7** Semi-logarithmic plots of $M_0/M_t$ vs. time for the removal of chlorine from PECH $[\text{PECH}]_0 = 0.05$ M; $[18\text{-}0\text{-}6]_0 = 0.25$ M. ($\blacktriangle$) 100°C; ($\bigcirc$) 140°C



**Figure 6** PMR spectra at 3–5 ppm in $d_5$-nitrobenzene $[\text{PECH}]_0 = 0.05$ M; $[18\text{-}0\text{-}6]_0 = 0.25$ M. (——) PECH before the onset of the reaction; (- - - -) after 6 h of fluorination at 140°C

**Table 3** Solubility of potassium halides in nitrobenzene in presence of 0.2 M 18–0–6 $T = 140°C$

| | Halide ion | |
|---|---|---|
| Solid phase | $F^-$ (mM) | $Cl^-$ (mM) |
| KF | 14.5 | — |
| KCl | — | 25.3 |
| KF + KCl | 15.4 | 25.3 |

slow-down in the reaction rate must, therefore, be attributed to the presence of fluorine substituted groups in the neighbourhood of the unsubstituted chlorine atoms. Please note that presence of only one neighbouring fluorine seems to be sufficient for inhibition of the reaction at 100°C, but two neighbouring fluorines seems to be required for such effect at 140°C.

What is the reason for this rather unexpected behaviour? Is it due to the decrease in polarization of the C–Cl bond caused by the introduction of an electron withdrawing fluorine atom? Such strong inductive effect seems to be unlikely in our system, since the two halogens are separated by four C–C bonds and by a strongly electronegative etheral group. Steric hindrance which prevents further reaction certainly cannot be considered for substitution of a large chlorine by a small fluorine atom. It seems, therefore, that the observed effect must be attributed to some kind of interaction between the covalently bonded fluorine and the fluorinating agent. A 'well' in the potential surface corresponding to the transient $K^+ F_2^-$ species was indeed predicted by Zeri and Shapiro[20]. A hypothetical complex: $C\text{-}F\text{··}F^-,K^+$ is analogous to such transient species. Thus, the approach of the KF (18-0-6) to the C–Cl site may be greatly slowed down by its interaction with a neighbouring C–F group. The validity of such explanation seems to be confirmed by results obtained when bis(chloroethyl)ether (BCE) has been reacted at 100°C under similar conditions. The g.c.–m.s. analysis of the reaction products shows that only one chlorine is substituted by fluorine in the $Cl\text{·}CH_2\text{·}CH_2\text{·}O\text{·}CH_2\text{·}CH_2\text{·}Cl$ molecule, although both chlorines are known to be highly active (cf. *Figure 8*). Clearly, introduction of one fluorine into BCE inhibits the substitution of the second chlorine atom. Plots of

$\ln(M_0/M_t)$ vs. time for reactions started with various concentrations of BCE are shown in *Figure 9*. Linearity of such plots for experiments conducted at relatively low initial concentration of BCE seems to point out to a pseudo first-order character of the reaction. This conclusion is, however, contradicted by the fact that the apparent rate constant of the reaction seems to increase when the initial concentration of BCE is decreased by a large factor. Thus, nearly five fold decrease of the apparent rate constant corresponds to a four fold increase in $[BCE]_0$. Moreover, when the concentration of BCE is very high ($[BCE]_0 = 2.5$ M), the plot of $\ln(M_0/M_t)$ vs. time deviates from linearity. It should be noted that the ratio between the fluorinating agent KF (18-0-6) whose concentration is fixed by 'crown' concentration, and the concentration of the C–F groups in the solution is strongly affected by changes in $[BCE]_0$. Thus, results obtained for BCE are consistent with our suggestion that the drastic slow down in fluorination of PECH at higher degree of conversion is due to interaction of the fluorinat-
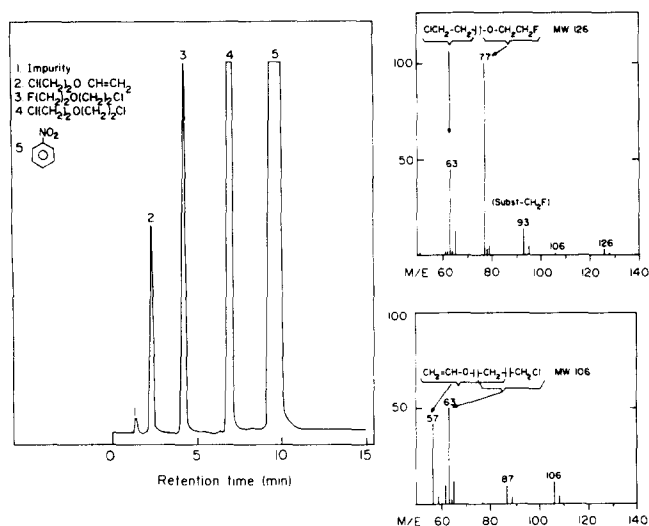
**Figure 10**

ing agent with the fluorinated product. Such interaction is also indicated by the observation, that isomerizations leading to formation of the thermodynamically more stable isomers of perfluorinated olefins are greatly enhanced, by the KF(18-0-6) complex in acetonitrile[21].

## REACTION MECHANISM

It has been pointed out in the preceding section that S/E ratio for PECH remains constant during the reaction (70/30) and is not affected by a change in temperature. Obviously, the energy of activation of the two processes must be virtually identical. Its value seems to be quite low ($\sim 5$ kcal mol$^{-1}$), since only two fold increase in the reaction rate is obtained when the temperature is raised from 100°C to 140°C. *Figure 10* is proposed to account for these experimental findings.

It is assumed that both reactions are preceded by formation of a transition state complex between the organic halide and the $F^-$, $K^+$ (18-0-6) and different modes of its decomposition provide pathways either for elimination or for substitution. Approach between $F^-$ and a hydrogen on $\beta$-carbon and the subsequent removal of a proton, followed by ejection of $Cl^-$, yields a product of an elimination. On the other hand, approach of the $F^-$ to the $\alpha$-carbon may push the $Cl^-$ towards the $K^+$ (18-0-6) and end up with a substitution of a chlorine by fluorine. It is assumed in this scheme that both $F^-$ and $K^+$ (18-0-6) play an active role in the formation of such transition state complex. This is supported by the experimentally observed large difference between the activity of $F^-$, $K^+$ (18-0-6) and of other alkali metal fluorides.

Only trace amounts of substitution and elimination products have been detected, after prolonged reaction times under our experimental conditions, when KF was replaced by NaF or RbF. The low reactivity of RbF can be perhaps explained by very low solubility of RbF and its 18-0-6 complex in nitrobenzene. Such excuse does not apply, however, to NaF. The equilibrium concentrations of NaF (15-0-5) and NaF (18-0-6) in solutions of the respective crown ethers in nitrobenzene are only a factor of 3.8 and 10, respectively, lower than the concentration of KF (18-0-6) in an analogous solution. The low activity of the sodium fluoride complex may be attributed either to low nucleophilicity of fluorine anion, strongly attracted by the relatively small sodium cation, or simply to the proximity of the two ions in the complex, which reduces drastically its ability to enhance the polarization of the C–Cl bond.

**Figure 8** G.c.–m.s. spectra of the products of reaction of BCE at 100°C; time=41 h, $[BCE]_0 = 2.5$ M; $[18-0-6]_0 = 0.5$ M. (a) G.c. spectrum: (1) impurity; (2) $ClCH_2CH_2OCH_2CH=CH_2$; (3) $ClCH_2CH_2OCH_2CH_2F$; (4) $ClCH_2CH_2OCH_2CH_2Cl$; (5) nitrobenzene. (b) M.s. of peak 2; (c) m.s. of peak 3
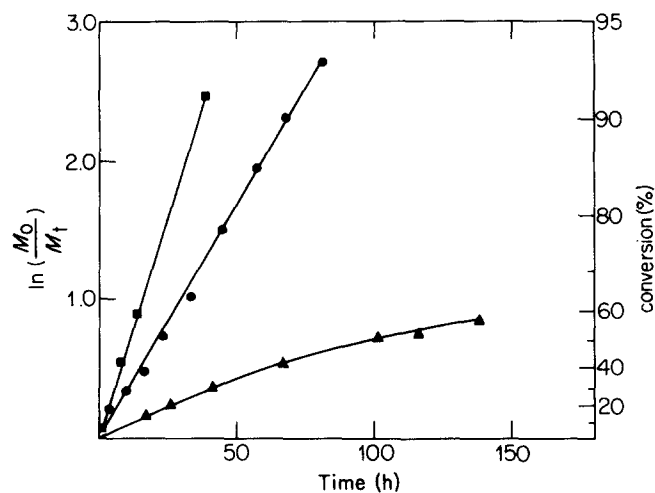
**Figure 9** Semi-logarithmic plots of $M_0/M_t$ vs. time for removal of chlorine from BCE in nitrobenzene at 100°C, $[18-0-6]_0 = 0.5$ M. (■) $[BCE]_0 = 2.5 \times 10^{-2}$M; (●) $[BCE]_0 = 2.5 \times 10^{-1}$M; (▲) $[BCE]_0 = 2.5$ M
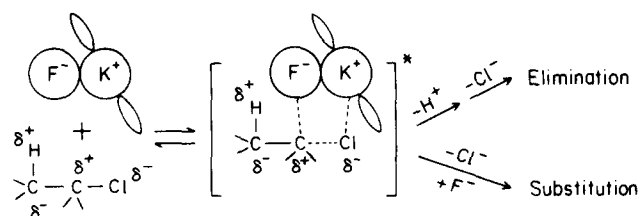
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