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Exchange of Halogens Between Aromatic Compounds in the Presence of Cu-HZSM-5 Zeolite

S. Imhaoulène, L. Vivier, M. Guisnet and G. Pérot*
URA CNRS 350 Catalyse en Chimie Organique 40, avenue du Recteur Pineau
86022 Poitiers Cedex France

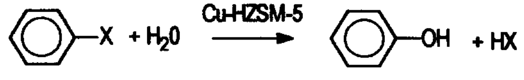
M. Gubelmann
Rhône-Poulenc Recherches, Centre d'Aubervilliers 93308 Aubervilliers France

Abstract : The reactions between various haloaromatics in binary mixtures which were approximately equimolar, were studied in gas-phase (673 K, atmospheric pressure) in the presence of a 2 wt % Cu-HZSM-5 zeolite. The exchange of halogens (ipso substitution) between the two compounds was assumed to occur either through a radical mechanism involving an electron transfer between an atom of copper (I) and one aromatic molecule or through a nucleophilic substitution involving arylcopper complexes as intermediates.

Introduction

Halobenzenes such as chloro- and bromobenzenes are among the cheapest and most reactive aromatic compounds. They can be used for the synthesis of phenol (1,2). However nowadays, the use of this reaction for the industrial synthesis of phenol seems to have lost its importance (2) but it can still be used for the synthesis of substituted phenols (3,4).

To perform the hydrolysis of halobenzenes (eq. 1) under optimal conditions, the use of catalysts like copper containing zeolites (5-8) is essential. The best catalysts have proved to be copper impregnated HZSM-5 zeolites (9).



(1)

X = Cl, Br

Two different mechanisms have been proposed : the nucleophilic aromatic mechanism (S_NAr) and the arynic mechanism (10). In order to understand the mechanism of hydrolysis, the reactivities of different monohalobenzenes were determined under the same conditions. The reactivity sequence was : ΦCl > ΦBr > ΦF (11) which was neither what was expected for a classical S_NAr mechanism, nor the one for an arynic mechanism. Consequently, it can be supposed that chloro- and bromobenzenes on the one hand, and fluorobenzene on the other, react through two different mechanisms. The hydrolysis of dihalobenzenes on CuHZSM-5 was carried out so as to obtain more information about the mechanism (11). To dispose of a common standard for comparison between the various dihalobenzenes the reaction was carried out in the presence of chlorobenzene. Thanks to these experiments (e.g. the hydrolysis of chlorobenzene in the presence of 3-bromofluorobenzene on Cu-HZSM-5) we discovered that an exchange between bromine and chlorine occurred simultaneously. We report here on this reaction which also occurs in the absence of water.

Experimental

Chemicals : all the chemicals were supplied by Rhône-Poulenc or purchased from Aldrich and were used without further purification. Their purety as checked by gas chromatography was generally of about 99%.

Catalysts : HZSM-5 (Si/Al ≈ 40) was synthesized according to the procedure described by Guth *et al* (12) using colloidal silica, sodium aluminate and tetrapropylammonium bromide. The sodium form of the zeolite was then exchanged with an ammonium chloride solution and calcined at 793K under dry air flow.

Cu-HZSM-5 (2 wt % Cu) catalysts were obtained by impregnation which was carried out by using 1 cm^3 of a 0.3 M aqueous solution of $Cu(NO_3)_2$ per gram of zeolite. Water was evaporated for 2h at 353K. The samples were dried then calcined at 773K under a dry air flow.

Procedure : the hydrolysis and/or exchange of the halobenzenes were carried out at 673K using a fixed-bed glass reactor. The standard operating conditions were 0.5 g of catalyst with a flow rate of a halobenzene mixture of 2 $cm^3.h^{-1}$.

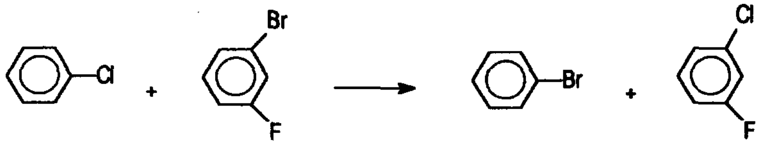
Samples of the reaction products containing two phases (organic and aqueous) were collected and dissolved in dimethoxyethane. The product distribution was determined by gas chromatography using a CPSil5 capillary column (25m, 0.12μm silicon film thickness). The identity of the products was determined by GC-MS analysis and by comparison of their retention times with those of commercial samples. The quantitative analyses were carried out with internal standard, usually one of the reactants. Reactants and products had very similar responses between 0.8 and 1. The calibration of the chromatograph was verified periodically by using mixtures made of commercial samples.

The chemical analysis of the catalysts was carried out by CNRS (Service central d'analyses, Echangeur de Solaize, BP22, 69390 Vernaison France).

Results

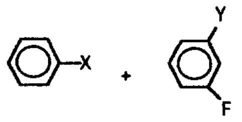
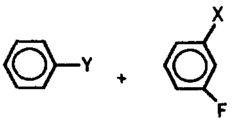
Under the conditions of the hydrolysis (at 673K, on Cu-HZSM-5, in the presence of water) we studied the exchange of halogen atoms between chlorobenzene and 3-bromofluorobenzene on one hand, and between bromobenzene and 3-chlorofluorobenzene on the other (eq. 2 and 3).

To ascertain which was the contribution of each catalyst constituent, the exchange reaction was carried out under the same conditions (at 673K, in the absence of water), without catalyst, in the presence of HZSM-5 or of Cu-HZSM-5. The results are reported in table 1.


(2)


(3)

Table 1 : Exchange reactions between halobenzenes at 673K in the absence of water.

reactants (50:50) 	catalysts	products (mol %)[a] 	
X = Cl , Y = Br (Eq 2)	none	2.5	2.5
	HZSM-5[b]	3.0	3.5
	Cu-HZSM-5	19.6	17.5
X = Br , Y = Cl (Eq 3)	none	1.2	1.2
	HZSM-5	1.0	1.0
	Cu-HZSM-5	13.2	14.3

[a] molar percentage of each product in the reaction mixture obtained from equimolar amounts of the reactants.
[b] in this case, 10% of isomerization of the disubstituted reactants into the 2- and 4- isomers was obtained.

Table 1 shows that the reaction was catalyzed by copper. Indeed, without a catalyst or in the presence of HZSM-5, there was less than 4% exchange. Under the same conditions the amount of product formed in the presence of Cu-HZSM-5 was greater for eq. 2 than for eq. 3 which shows that the exchange between chlorobenzene and 3-bromofluorobenzene was easier than the exchange between bromobenzene and 3-chlorofluorobenzene. There was no exchange with fluorine.

Figure 1 shows that water had no significant effect on the exchange reaction. The only difference between the two experiments is that there was a greater amount of phenol formed by hydrolysis with the experiment with water.

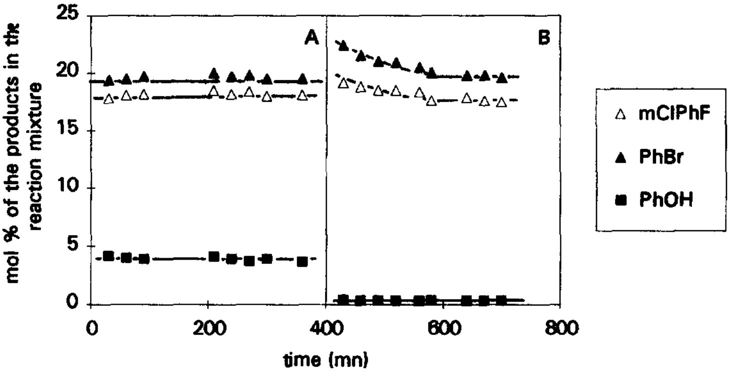


Figure 1 : Transformation of the mixture : chlorobenzene and 3-bromofluorobenzene in the presence (A) and in the absence (B) of water (1mol/mol halobenzene), on Cu-HZSM-5 at 673 K. (mClPhF = 3-chlorofluoro-benzene, PhBr = bromobenzene, PhOH = phenol).

The effect of contact time was studied under the same conditions with different weights of catalysts and/or flow rates. Figure 2a shows the transformation of the mixture at low contact times. It can be seen that at low conversion, the exchange is proportional to the contact time. Figure 2b shows the effect of contact time in a larger range indicating that the exchange reaches an equilibrium : the mixture is composed at this stage of about 25% of each compound. The same equilibrium is reached with mixtures of 3-bromofluorobenzene plus chlorobenzene on one hand (figure 2) and of 3-chlorofluorobenzene plus bromobenzene on the other (not shown).

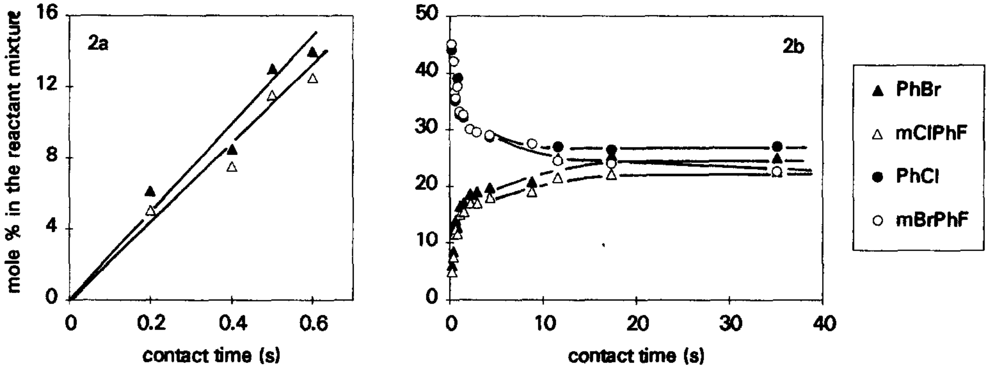
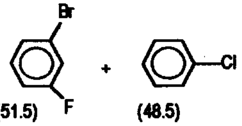
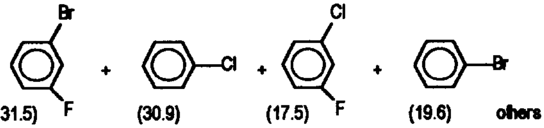
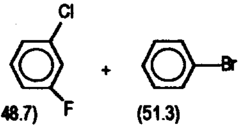
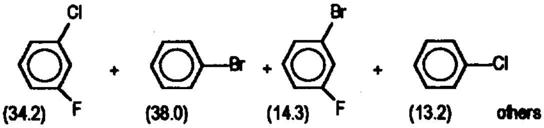
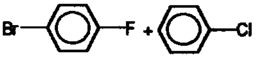
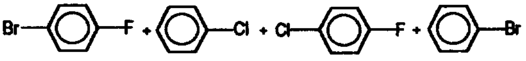
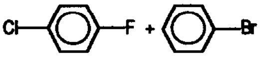
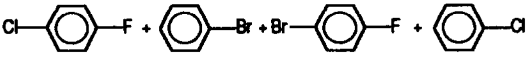
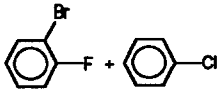
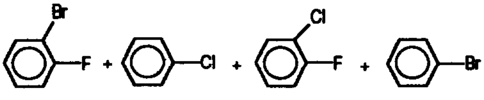
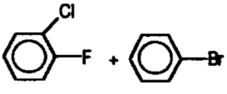
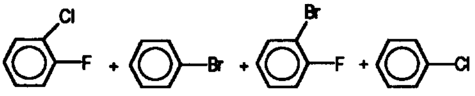
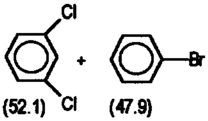
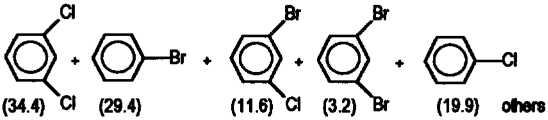
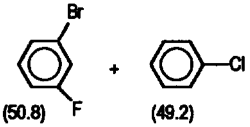
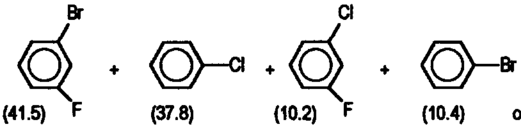
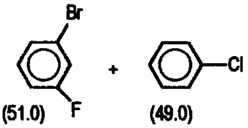
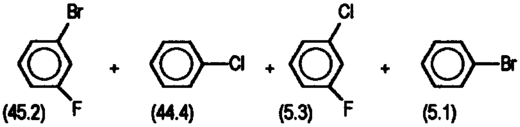


Figure 2 : Effect of contact time on the transformation of a mixture of 3-bromofluorobenzene and chlorobenzene over Cu-HZSM-5. (PhBr = bromobenzene, mClPhF = 3-chlorofluorobenzene, PhCl = chlorobenzene, mBrPhF = 3-bromofluorobenzene).

Table 2 : Exchange of halogen atoms between different disubstituted benzenes and chloro- or bromobenzene on Cu-HZSM-5 in the absence of water.

exp	reactants (mol %)	reaction mixture (mol %)
1	 (51.5) (48.5)	 (31.5) (30.9) (17.5) (19.6) others (0.5)
2	 (48.7) (51.3)	 (34.2) (38.0) (14.3) (13.2) others (0.3)
3	 (59.0) (41.0)	 (39.8) (25.4) (14.1) (15.7) others (5.0)
4	 (50.1) (49.9)	 (39.9) (39.0) (9.7) (10.1) others (1.3)
5	 (46.3) (53.7)	 (28.3) (34.3) (18.4) (18.0) others (1.0)
6	 (51.3) (48.7)	 (38.5) (36.8) (11.2) (11.7) others (1.8)
7	 (52.1) (47.9)	 (34.4) (29.4) (11.6) (3.2) (19.9) others (1.5)
8[a]	 (50.8) (49.2)	 (41.5) (37.8) (10.2) (10.4) others (0.1)
9[ab]	 (51.0) (49.0)	 (45.2) (44.4) (5.3) (5.1)

[a] CuHZSM-5 (50mg) with a flow rate of a halobenzene mixture of 2 $cm^3.h^{-1}$.

[b] with added nitrobenzene (23 mol%).

Various disubstituted benzenes were reacted with chlorobenzene or bromobenzene under standard conditions. The results are summarized in table 2.

In all the cases, the main reaction is the exchange of halogen atoms. A small amount of isomerization of the disubstituted benzenes also occurs (isomers designated as "others"in table 2). However, what is most striking is that the exchange reaction is almost 100 % regioselective : 3-bromofluorobenzene gives 100 % 3-chlorofluoro-benzene (exp. 1) and vice versa (exp. 2).

If we compare the behaviour between 2-, 3- and 4-bromofluorobenzenes in exchange with chlorobenzene (exp. 5, 1 and 3 respectively) on the one hand, or between 2-, 3- and 4-chlorofluorobenzenes in exchange with bromobenzene (exp. 6, 2 and 4 respectively) on the other, it appears that 3-isomers are slightly more reactive than 2- and 4- isomers.

The reaction of bromobenzene with 1,3-dichlorobenzene leads to a mixture of 3-bromochlorobenzene, 1,3-dibromobenzene and chlorobenzene (exp. 7), which means that 1,3-dichlorobenzene undergoes two successive exchange reactions with bromobenzene.

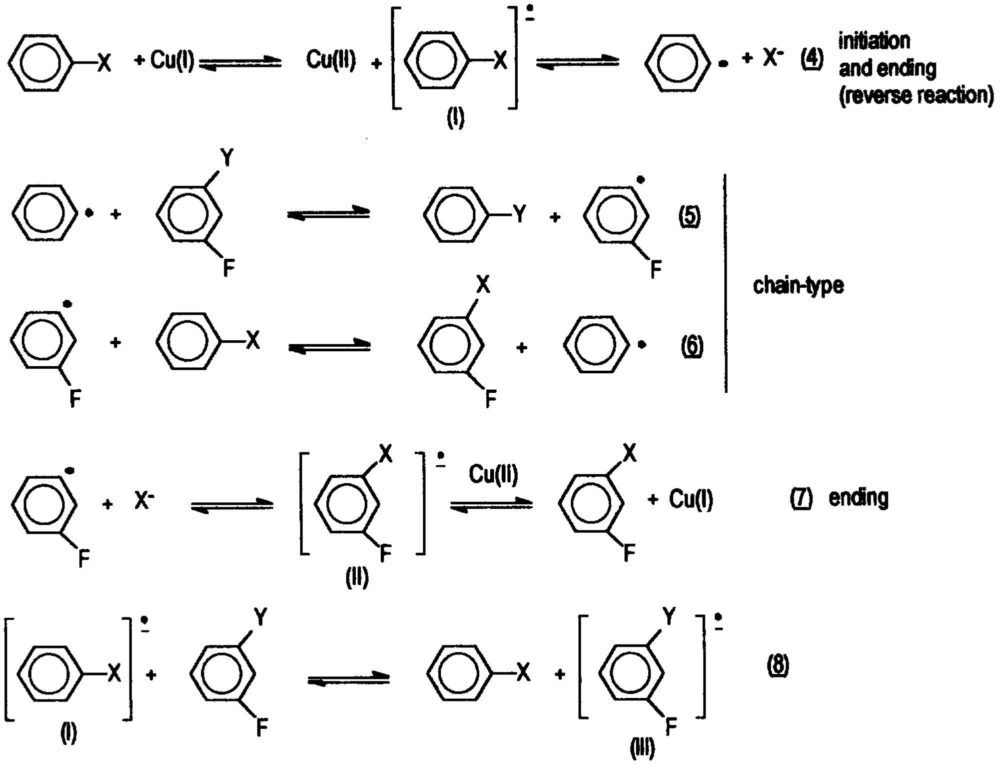
Discussion

The exchange of halogens between aromatic compounds promoted by copper (I) or (II) (13-15), by nickel (I) or (II) (16-18) or by a phase-transfer catalyst (19) has already been reported. The reactions of this type were originally conducted photochemically (20, 21). Generally, they proceeded by exchange of an halogen atom from an aromatic compound (usually bromobenzene) with another halogen atom (usually chlorine) coming from various inorganic sources (OCl^- (18, 19), CuCl (13-15), $NiCl_2$ (16), arylnickelchloride (16, 17)...).

The ease of displacement of halogen atoms from aromatic nuclei is in the order : I > Br > Cl >> F (14, 15). The displacement of fluorine does not occur as shown previously for hydrolysis (11) and as reported in the literature concerning the exchange with other halogens (14, 22). This is the opposite order of the sequence obtained in S_NAr reactions and corresponds to the reactivity sequence which is generally obtained in $S_{RN}1$ reactions (22).

A reaction very similar to the one we obtain was reported by Tsou and Kochi (17). An exchange of halogen atoms occurred between 4-bromomethoxybenzene and iodobenzene to give 4-iodomethoxybenzene and bromobenzene in the presence of nickel (I). An equilibrium was reached in which there was about 25 % of each arylhalide. According to the authors, this exchange reaction most likely proceeded via free-radical ipso-substitution. According to our results a mechanism similar to the one proposed by Bunnett (22) can be proposed for the exchange of halogen atoms between two different aromatic compounds catalyzed by Cu(I)-zeolite (scheme 1). ESCA results ($Cu2p^{3/2}$ binding energy : 932.5 eV, no satellite ; Auger parameter : 1847.7 eV) seem to indicate that Cu(I) species are actually present on the catalyst surface (23). As reported by several authors (24-27) Cu(II) when deposited on zeolites in particular can undergo autoreduction when treated at temperatures above 573 K even in the absence of a reducing gas.

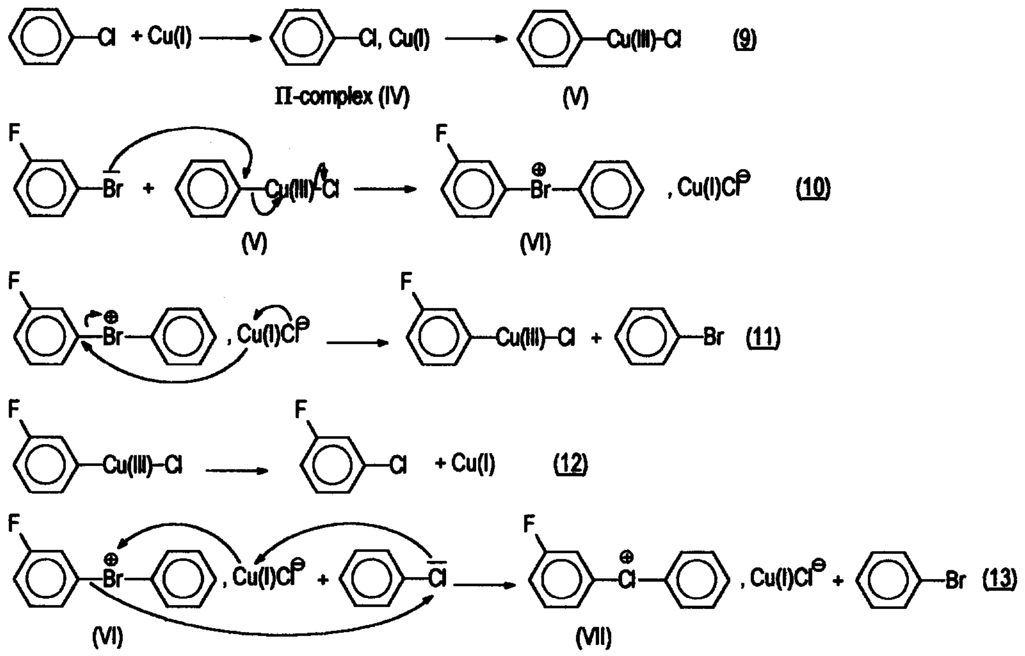
Scheme 1 - Mechanism of exchange reactions by radical anions intermediates.

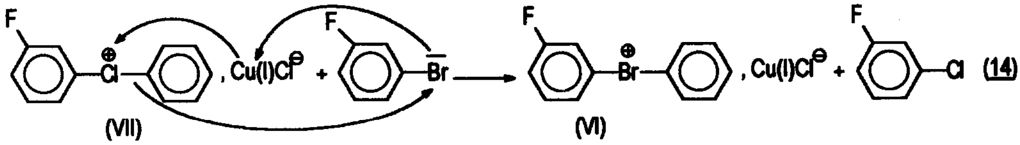


As indicated in scheme 1, the metal operates as a one-electron donor as in the $S_{RN}1$ reaction. The first step is a reduction of the aromatic compound, followed by a homolytic carbon-halogen (Br or Cl) bond scission to form an aryl radical and a halogen ion X^- which is relatively stable according to its electronic structure (eq. 4). The halogen atom transfer occurs through a chain type reaction between the radical and another haloaromatic molecule (eq. 5 and 6). Ending of the chain process can occur by any reaction between two radicals or between a radical and an anion as in the reverse of the initiation step (eq. 4) or in eq 7. Another reaction step (eq. 8) which may be involved is the electronic transfer between the radical-anion (I) and the second haloaromatic reactant to give another radical-anion (III). This means that depending on its reducibility either of the substrates can initially react with copper. The fact that the reactivity sequence in similar reactions is I > Br > Cl >> F may reflect the reducibility of the various elements if as is generally assumed the first step of reaction 4 in scheme 1 is the rate-limiting step (28). Bunnett (29) explains the difference between the reactivities of halogen atoms by the strengths of the several C-X bonds which are consequences of the electron transfers into C-X σ^* MOs, inasmuch as the energy levels of the latter increase in the order iodine < bromine < chlorine.

The addition of nitrobenzene (23 mol%) to the reaction mixture of chlorobenzene and of 1,3-bromofluorobenzene decreases the conversion which is divided by 2 (exp. 8 and 9 table 2). This is in favour of the involvement of radicals in the rate-limiting step of the reaction (29). However the effect is not significant enough to exclude the possibility of a mechanism in which radicals would not exist as free species. Hence a mechanism involving aryl copper complexes as suggested by several authors in similar cases (15, 30, 31) can be considered (scheme 2). This mecanism can be considered as a Cu assisted S$_N$Ar reaction involving a two electron transfer instead of a one electron transfer as in the foregoing mechanism. According to this mechanism (described here for the reaction between chlorobenzene and 1,3-bromofluorobenzene) a Cu-complex would be formed through reaction between Cu(I) and chlorobenzene (eq. 9), followed by a nucleophilic attack of (V) by 1,3-bromofluorobenzene (eq. 10) leading to (VI). Through the reverse process, (VI) can generate bromobenzene (eq. 11) and then 1,3-chlorofluorobenzene can be produced (eq. 12). It can also be considered that (VI) could in fact act as the actual catalyst as indicated in eq. 13 and 14. In the case described here Cl$^-$ in complex (VI) would remain adsorbed on the catalyst while additional chlorobenzene molecules would enter the cycle to produce 1,3-chlorofluorobenzene (eq. 13), and 1,3-bromofluorobenzene to produce chlorofluorobenzene (eq. 14) and eventually regenerate (VI).

scheme 2 - Mechanism of exchange reactions by Cu-complex intermediates.





(14)

Our results show that 3-bromofluorobenzene is about 1.5 times more reactive towards chlorobenzene than 3-chlorofluorobenzene towards bromobenzene (table 2, exp. 1 and 2). In these two cases, there are carbon-chlorine and carbon-bromine bond scissions. Again in the case of $S_{RN}1$ mechanism, if the first step of reaction 4 is the rate-limiting step of the exchange process this would mean that bromine is more easily reduced than chlorine and that this lability is enhanced by fluorine on the same nucleus.

Due to the presence of two atoms of chlorine 1,3-dichlorobenzene has two possibilities for reacting with bromobenzene while 3-chlorofluorobenzene has only one. Taking this into account, if we compare the formation of chlorobenzene in exp. 2 and in exp. 7 1,3-dichlorobenzene is apparently less reactive than 3-chlorofluorobenzene. This means that fluorine which is more electronegative than chlorine, has a stronger promoting effect on the reducibility of the other halogen of the same nucleus.

Conclusion

Copper in the zeolite is an efficient promoter of halogen exchange between two aromatic compounds. The regioselectivity suggests an ipso-substitution either through a mechanism in which copper (I) undergoes an oxidation reaction leading to the formation of aryl radicals and halogen ions or through a substitution mechanism involving arylcopper complexes as intermediates.

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