THE REACTION OF ATOMIC FLUORINE WITH FLUOROBENZENE

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SUMMARY

The reaction of atomic fluorine with fluorobenzene under cold plasma conditions leads to the formation of three difluorobenzene isomers. The isomer distributions confirm the selective introduction of atomic fluorine into the aromatic ring as previously found in the reaction of atomic fluorine and bromobenzene. A comparison of the isomer distribution indicates that the presence of a fluorine atom in a ring has greater inhibiting effect on *ortho* substitution than the corresponding bromine atom.

INTRODUCTION

Direct introduction of fluorine into an aromatic ring without corresponding loss of aromaticity has been an unsolved problem for years. Early attempts at direct fluorination led to explosions, the only products being tars[1-3]. Having obtained only a polymer, Bockemüller concluded that under the conditions for direct liquid-phase fluorination aromatic compounds form addition products or polymers instead of the desired substitution products. In 1969, Grakauskas[5] reported the direct liquid-phase fluorination of benzene, toluene, bromobenzene and several other aromatic compounds. Based on the distribution of *ortho, meta* and *para* isomers of the monosubstituted fluorobenzenes, an ionic electrophilic substitution mechanism has been proposed for these reactions.

Recently, the first substitution of fluorine into an aromatic ring by direct reaction with atomic fluorine generated in an electrodeless radiofrequency glow discharge has been reported[6]. Bromobenzene was reacted with atomic fluorine to produce three fluorobromobenzene isomers, fluorobenzene and three difluorobenzene isomers. The isomer distribution of the products indicated that the introduction of fluorine into an aromatic ring *via* a radical mechanism can occur

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with much more selectivity than was previously thought. Thus selective substitution alone is not a sufficient criterion for proposing an ionic mechanism. The purpose of this paper is to report a second example of the selective introduction of the fluorine atom into an aromatic ring utilizing atomic fluorine generated in an electrodeless radiofrequency glow discharge.

RESULTS AND DISCUSSION

As in the previous study, the undiluted elemental fluorine was passed through an electrodeless radiofrequency discharge resulting in the red glow characteristic of neutral fluorine atoms[7]. The fluorine then encountered a stream of fluorobenzene outside the discharge region. Table 1 presents the experimental conditions and results obtained in a series of eight reactions. The products of the reactions consisted of a mixture of fluorobenzene, three difluorobenzene isomers, polymer

TABLE 1

REACTION CONDITIONS AND YIELDS

Reaction	Time (min)	Temperature (°C)	Ratio F_2/C_6H_5F	%C_6H_5F unreacted	%Yield fluorinated products	%Yield polymer and gases
A	207	0	3.78	1.39	5.4	94.2
B	190	10	1.89	55.2	9.0	36.6
C	256	0	2.84	31.4	12.3	61.6
D	261	0	3.47	42.5	14.6	43.9
E	195	0	3.50	26.5	13.7	62.5
F	319	0	4.33	26.9	11.3	62.6
G	268	0	5.97	19.7	10.1	73.2
H	480	0	7.59	0.5	0.9	98.9

TABLE 2

ISOMER DISTRIBUTION OF THE DIFLUORINATED PRODUCTS*

Reaction	Isomer distribution (%)			Relative ratio
	ortho	meta	para	$o : m : p$
A	1.11	1.50	2.76	1.00 : 1.35 : 2.49
B	1.74	2.19	5.08	1.00 : 1.26 : 2.92
C	3.49	2.42	6.34	1.44 : 1.00 : 2.62
D	3.82	2.87	7.86	1.33 : 1.00 : 2.74
E	5.09	2.56	6.11	1.99 : 1.00 : 2.39
F	3.19	1.91	6.16	1.67 : 1.00 : 3.23
G	2.74	2.09	5.31	1.31 : 1.00 : 2.54
H	0.28	0.27	0.37	1.04 : 1.00 : 1.37

* Normalized to exclude polymers and gases.

and non-condensable gases. The isomer distribution of the difluorinated products is shown in Table 2.

Reaction A in Table 1 represents the control reaction between fluorine and fluorobenzene in the absence of the radiofrequency discharge. As observed in the reaction of molecular fluorine and bromobenzene, the major product is a polymer. Only about 5.4% of the fluorobenzene reacted to form fluorinated aromatic compounds.

The maximum conversion to the difluorobenzene isomers seems to occur at a mole ratio of *ca.* 3.5:1.0 of fluorine to fluorobenzene. Table 1 discloses that higher fluorine to fluorobenzene ratios result in the formation of a greater proportion of non-recoverable products. For example, in reaction H with a fluorine to fluorobenzene ratio of 7.6:1.0 only about 1% of the fluorobenzene was converted to condensable products; the remainder reacted to form polymeric material and non-condensable gases.

As in the reaction of bromobenzene and atomic fluorine[6], the product isomer distribution for the difluorobenzenes in the series of reactions follows the general pattern *para*>*ortho*>*meta*. For each reaction, the distribution amongst the isomers seems to indicate selective *para* substitution by the fluorine. Selective fluorine substitution *via* a radical mechanism has also been demonstrated in the isomer distribution of the products formed by the vapor-phase fluorination of benzene and nitrobenzene with xenon difluoride[8]. For benzene, MacKenzie and Fajer found that once the fluorine atom is substituted in the aromatic ring, *para* orientation is then favored. The fluorine atom in the ring also appears to show as great an inhibiting effect for *ortho* as for *meta* substitution. In the reaction between fluorobenzene and atomic fluorine, *ortho* substitution appears to be inhibited. This is especially evident when compared to the isomer distribution for the bromo-benzene and atomic fluorine reaction where the average relative ratio of *ortho* to *meta* product for the fluorobromobenzene isomers is 2.4:1.0 and 2.2:1.0 for the difluorobenzene isomers. In contrast, in the reaction of fluorobenzene and atomic fluorine the average relative ratio of *ortho* to *meta* product for the difluoro-benzenes is 1.5:1.0.

From the three sets of average relative ratios for the *ortho* to *meta* product distribution, it is possible to form some conclusions concerning the mechanism of the bromobenzene and atomic fluorine reaction. The formation of fluorobenzene and the three difluorobenzene isomers has been accounted for by a reaction involving an exchange between halogen molecules and aromatic halides[9-11]. The proposed intermediate[12] corresponds to the " π complexes " discussed by Brown in regard to electrophilic substitution. The intermediate involves a fluorine atom which is not bonded to any particular carbon atom but is associated with, and undergoes electron transfer from, the entire π-electron system.

The sequence of reactions in which the difluorobenzene isomers are formed from bromobenzene may be represented by

$$C_6H_5Br + F\bullet \rightarrow C_6H_5F + Br\bullet \tag{1}$$

$$C_6H_5F + F\bullet \rightarrow C_6H_4F_2 + H\bullet \tag{2}$$

or

$$C_6H_5Br + F\bullet \rightarrow C_6H_4BrF + H\bullet \tag{3}$$

$$C_6H_4BrF + F\bullet \rightarrow C_6H_4F_2 + Br\bullet \tag{4}$$

If the predominant mechanism for the formation of difluorobenzene is that depicted in equations (1) and (2), then the ratio of *ortho* to *meta* product distribution should be approximately that obtained in the reaction of fluorobenzene and atomic fluorine (1.5:1.0) where the fluorine atom in the ring inhibits the formation of the *ortho* isomer. However, if the predominant mechanism for the formation of the difluorobenzenes is that depicted in equations (3) and (4), then the ratio of *ortho* to *meta* product distribution should be about the same as that obtained for the fluorobromobenzenes, *i.e.* 2.4:1.0. From the observed ratio of *ortho* to *meta* product distribution of 2.2:1.0, it appears that the latter mechanism is predominant.

The isomer distribution of the products in the reaction of fluorobenzene and atomic fluorine confirms the selective nature of the introduction of atomic fluorine into the aromatic ring as previously found in the reaction of atomic fluorine and bromobenzene. Comparison of the isomer distributions indicates that the introduction of a fluorine atom into the ring has a greater inhibiting effect on *ortho* substitution than the corresponding bromine atom. Further studies are being at present conducted to determine the effects of other ring substituents on the introduction of atomic fluorine into the ring.

EXPERIMENTAL

The experimental apparatus and procedures were the same as those described previously[6] where the complete experimental details may be found.

The reaction products were analyzed by gas chromatography, using a 8 mm × 5.22 m column containing 10% Carbowax 20M on Chromosorb W (60/100 mesh)[13,14]. The retention times of the fluorobenzene and the three difluorobenzene isomers were identical with those of the authentic compounds. Peak areas were obtained using a Disc integrator and then compared with calibration curves obtained using injections of authentic compounds of known concentration. In this manner, yields and isomer ratios were determined.

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