

RADIOFREQUENCY FLUORINATION OF BROMOBENZENE USING ELEMENTAL FLUORINE

ANNA HARKINS VASEK* AND LEWIS C. SAMS

Department of Chemistry, Texas Woman's University, Denton, Texas 76204 (U.S.A.)

(Received April 10, 1972)

SUMMARY

Passage of undiluted elemental fluorine gas through a radiofrequency discharge region is known to produce atomic fluorine. Reaction of atomic fluorine with bromobenzene vapor gave the corresponding bromofluorobenzene isomers and small amounts of fluorobenzene and difluorobenzene isomers. From the isomer distributions the substitution of the atomic fluorine is observed to be more selective than previously thought.

INTRODUCTION

Until recently little research has been done in the area of direct fluorination of organic compounds. Thermochemical data showing the great reactivity of molecular fluorine, which results in very high heats of reaction, was used to explain the failure of the attempts at direct fluorination¹. In 1961, Grakauskas reported the first in a series of papers on direct liquid-phase fluorinations². Recently, an excellent review of Grakauskas's direct liquid-phase fluorination techniques has been published³. Grakauskas's success with direct liquid-phase fluorinations encouraged this laboratory in its studies of possible direct fluorination techniques for aromatic compounds.

During this same period, several papers concerning the reactions of halo-benzenes in radiofrequency glow discharges appeared. Stille and Rix⁴ studied the decomposition of chlorobenzene and the three dichlorobenzene isomers in a glow discharge. The same report also investigated the reaction between a chlorine gas

* Robert A. Welch Postdoctoral Fellow 1971-72. Present address: University of Texas Southwestern Medical School, Dallas, Texas (U.S.A.).

plasma and chlorobenzene, and the reaction of a chlorobenzene plasma with both chlorine gas and bromine vapor. The major products of the reaction between the chlorine gas plasma and chlorobenzene were benzene, chlorobenzene and the three dichlorobenzene isomers. Fridmann and Dinan⁵ also published a report of the synthesis of chlorobenzene from the reaction of elemental chlorine gas and bromobenzene in an electrodeless radiofrequency glow discharge. These studies, along with several later papers^{6,7,8} which demonstrated the non-thermal generation of atomic fluorine using low-pressure electrodeless electrical discharges, led to the following investigation. The purpose of this paper is to report the first substitution of fluorine into an aromatic ring by direct reaction with atomic fluorine generated in an electrodeless radiofrequency glow discharge.

RESULTS AND DISCUSSION

In the present study, the passage of undiluted elemental fluorine through an electrodeless radiofrequency discharge results in the red glow characteristic of neutral fluorine atoms⁹. The fluorine then encounters a stream of bromobenzene outside the discharge region. The experimental conditions and results of a series of six runs are presented in Table 1. The products of the reactions are a mixture of bromobenzene and three bromofluorobenzene isomers, small amounts of fluorobenzene and the three difluorobenzene isomers, polymer and non-condensable gases. The distribution of the fluorinated products is presented in Table 2.

Run A in Table 1 represents the control reaction of fluorine and bromobenzene in the absence of the radiofrequency discharge. Without the radiofrequency discharge, the major product between molecular fluorine and bromobenzene was found to be a polymer. Only about 5.5 per cent of the bromobenzene reacted to form fluorinated aromatic compounds; this reaction also had the lowest percentage recovery of unreacted starting material, namely 10%.

TABLE 1
REACTION CONDITIONS AND YIELDS

Run	Time (min)	Temperature (°C)	Ratio F ₂ /C ₆ H ₅ Br	% C ₆ H ₅ Br unreacted	% Yield fluorinated products	% Yield polymer and gases
A	130	0	2.0	10.0	5.5	84.5
B	170	0	1.2	51.1	8.4	40.5
C	265	25	3.9	45.5	10.0	44.5
D	280	0	4.4	30.3	15.7	54.0
E	180	0	5.7	20.1	20.0	59.9
F	80	0	5.7	50.1	22.1	27.8

TABLE 2
 PRODUCT DISTRIBUTIONS

Run	C ₆ H ₄ F ₂ *			Rel. ratio <i>o:m:p</i>	C ₆ H ₄ BrF*			Rel. ratio <i>o:m:p</i>	C ₆ H ₅ F* % Yield
	Isomer distribution, %				Isomer distribution, %				
	<i>ortho</i>	<i>meta</i>	<i>para</i>		<i>ortho</i>	<i>meta</i>	<i>para</i>		
A	0.25	0.17	0.34	1.4:1:2	4.80	3.26	3.61	1.5:1:1.1	0.48
B	0.06	0.03	0.08	2.5:1:3.0	3.73	1.79	5.80	2.1:1:3.2	0.12
C	0.09	0.04	0.13	2.2:1:3.4	3.52	1.53	4.75	2.3:1:3.1	0.16
D	0.15	0.07	0.27	2.3:1:4.0	8.50	3.30	8.64	2.5:1:2.6	0.24
E	0.38	0.17	0.59	2.2:1:3.4	7.96	4.16	10.01	1.9:1:2.4	0.32
F	0.13	0.06	0.15	1.9:1:4.3	12.0	3.79	12.60	3.1:1:3.3	0.23

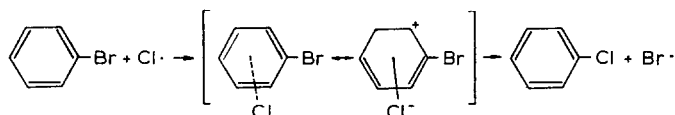
* Normalized to exclude polymer and gases.

Passage of the fluorine through the radiofrequency discharge prior to its reaction with bromobenzene decreases the percentage conversion to polymer and also increases the formation of the bromofluorobenzenes and fluorobenzenes. The yields of the bromofluorobenzenes and fluorobenzenes have been found to vary directly with the amount of fluorine. The maximum yields of the bromofluorobenzenes and fluorobenzenes are observed for the reaction with the highest fluorine to bromobenzene mole ratio (5.7). On the other hand, the percentage conversion to polymer and the percentage unreacted bromobenzene did not show a correlation with the millimoles of fluorine used.

The product isomer distribution for both the bromofluorobenzenes and the difluorobenzenes in the series of reactions appears to follow a uniform pattern with *para* > *ortho* > *meta* substitution. These distributions are tabulated in Table 2. For each run, the distribution among isomers seems to indicate a selective substitution by the fluorine; this is especially evident when allowance is made for the two *ortho* and *meta* positions as opposed to the single *para* position. Selective substitution in a radical-mechanism fluorination has been demonstrated in the isomer distribution of the products formed by the vapor-phase fluorination of benzene and nitrobenzene with xenon difluoride¹⁰. From their data, MacKenzie and Fajer concluded that for nitrobenzene the significant *meta* substitution was a result of the *meta* orientating effect of the NO₂ group. For benzene, they found once the fluorine atom was substituted on the aromatic ring, *para* orientation was then favored. The fluorine atom on the ring also appeared to show as great an inhibiting effect for *ortho* as for *meta* substitution. In the case of a bromine atom on the ring, we observed that *para* orientation is again favored, but that unlike the fluorine atom the bromine atom did not appear to inhibit *ortho* substitution to the same extent as it inhibited *meta* substitution.

The formation of the fluorobenzenes can be accounted for by a little known reaction, the exchange between halogen molecules and aromatic halides. Eibner¹¹

was the first to note that when bromobenzene is treated with chlorine at room temperature in the absence of halogen carriers (*e.g.*, FeCl_3) chlorobenzene and bromine are produced. A number of halogen-substituted bromobenzenes exchange similarly¹². Walling¹³ proposed an intermediate corresponding to the " π complexes" discussed by Brown¹⁴ in regard to electrophilic substitution. This intermediate involves a chlorine atom which is not bonded to any particular carbon atom but is associated with, and undergoes electron transfer from, the entire π -electron system.



For the first time, a fluorine atom has been substituted into a benzene derivative with a direct fluorination method utilizing atomic fluorine in a gas-phase reaction. The isomer distribution of the products indicates the introduction of atomic fluorine into the ring occurs with much more selectivity than was previously thought. In the light of the isomer distribution obtained, it is possible that some of the direct liquid-phase fluorinations¹⁷ may be attributed to a radical mechanism instead of the electrophilic mechanism proposed.

Generation of atomic fluorine in an electrodeless radiofrequency glow discharge provides a convenient and relatively safe method for investigating the reactions of atomic fluorine with various organic substrates. Studies of this type are presently being continued in this laboratory.

EXPERIMENTAL

The plasma reactor (Fig. 1) was made of Pyrex glass. The reactor was activated inductively with an R.F. generator (Johnson Viking Model II) with deliverable power from minimum up to 180 W. The experimental set-up also

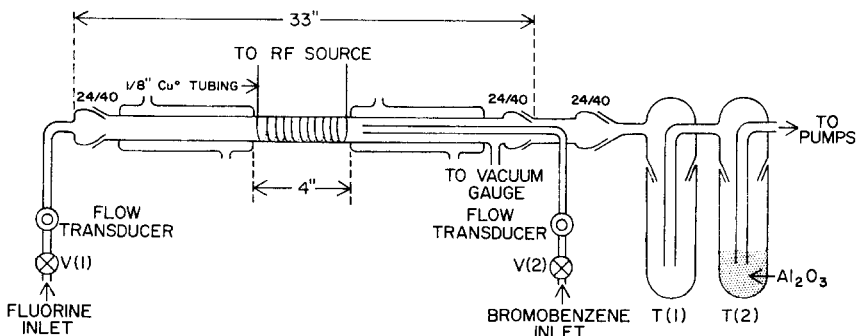


Fig. 1. A semi-schematic diagram of the discharge assembly utilizing an inductive discharge coil.

contained a Johnson Viking impedance matching box. All experiments were carried out at a radiofrequency of 29.1 MHz. Trap T(1) was cooled with liquid nitrogen. Trap T(2) contained activated alumina to prevent any corrosive fluorine gas from reaching the pumps. The fluorine gas and the bromobenzene vapor used throughout were measured by means of Hasting Mass Flowmeters Model LF-100 which were equipped with Monel metal fittings.

In operation, the system was evacuated to 2.5×10^{-2} Torr, then the R.F. generator was energized and the activator tuned while adjusting for maximum glow. The flow rate of the elemental fluorine was then regulated with a Hoke Micro-mite valve V(1) while the activator was tuned to maintain a glow discharge. The bromobenzene vapor was bled in through a similar valve V(2) downstream from the discharge region. The net power delivered by the generator is a function of gas type and concentrations, which in turn are related to system pressures and flow rates.

The gas chromatographic analysis of the mixture from T(1) was obtained using a 8 mm \times 5.22 m 10% Carbowax 20M on Chromosorb W (60/100 mesh) column^{15,16}. The retention times of the fluorobenzene and the three difluorobenzene isomers were identical with those of the authentic compounds. The three bromofluorobenzene isomers were identified from the infrared spectra of the fractions collected from the gas chromatographic analysis, and by the GLC retention times of the authentic compounds. Peak areas were obtained using a Disc integrator and then compared to calibration curves which were obtained by using injections of known concentration. In this manner, yields and isomer ratios were determined.

ACKNOWLEDGMENT

The generous support of this investigation by The Robert A. Welch Foundation is gratefully acknowledged. We also acknowledge the aid of Drs. Millie H. Wiley and James E. Johnson.

REFERENCES

- 1 J. A. YOUNG, *J. Chem. Educ.*, **47** (1970) 733.
- 2 V. GRAKAUSKAS, *Abstracts of the 140th National Meeting of the Amer. Chem. Soc., Chicago, Ill., Sept. 1961*, p. 23M.
- 3 V. GRAKAUSKAS, *Intra-Sci. Chem. Reports*, **5** (1971) 85.
- 4 J. K. STILLE AND C. E. RIX, *J. Org. Chem.*, **31** (1966) 1591.
- 5 S. FRIDMANN AND F. J. DINAN, *J. Org. Chem.*, **33** (1968) 1253.
- 6 N. VANDERKOOI AND J. S. MACKENZIE, *Adv. Chem. Ser.*, **36** (1962) 98.
- 7 D. E. ROSNER AND H. D. ALLENDORF, *J. Phys. Chem.*, **75** (1971) 308.
- 8 R. J. MCINTYRE AND F. K. MCTAGGART, *Austral. J. Chem.*, **24** (1971) 2683.
- 9 H. E. RADFORD, V. W. HUGHES, AND V. BELTRAN-LOPEZ, *Phys. Rev.*, **123** (1961) 153.
- 10 D. R. MACKENZIE AND J. FAJER, *J. Amer. Chem. Soc.*, **92** (1970) 4994.
- 11 A. EIBNER, *Ber.*, **36** (1903) 1229.
- 12 W. V. VOEGTLI, H. MUHR AND P. LAUGER, *Helv. Chim. Acta*, **37** (1954) 1627.
- 13 C. WALLING, *Free Radicals in Solution*, Wiley, New York, 1957, p. 312.

- 14 H. C. BROWN AND D. J. BRADY, *J. Amer. Chem. Soc.*, 74 (1952) 3570.
- 15 K. E. SEILER, M. A. DURRANCE AND L. C. SAMS, *J. Chromatog.*, 63 (1971) 375.
- 16 K. E. SEILER AND L. C. SAMS, *J. Chromatog.*, 69 (1972) 363.
- 17 V. GRAKAUSKAS, *J. Org. Chem.*, 35 (1970) 723.