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Reaction of Atomic Fluorine with Benzotrifluoride

Cynthia L. Jeffrey and Lewis C. Sams*

Department of Chemistry, Texas Woman's University, Denton, Texas 76204

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A radio-frequency excited plasma has been used to generate atomic fluorine. Using a molecular beam type of reactor, monofluorination of benzotrifluoride has been achieved with yields up to 28.3%. The atomic fluorine to benzotrifluoride ratio has been found to determine which isomer(s) will be produced and to control the total overall yield of monofluorinated products.

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, Bockemuller[4] 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 was proposed for these reactions.

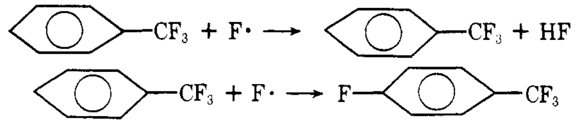
Recently, substitution of fluorine into an aromatic ring by direct reaction with atomic fluorine generated in an electrodeless radio-frequency glow discharge has been reported.[6,7] The isomer distribution of the products indicated that the introduction of fluorine into an aromatic ring via radical mechanism can occur with much more selectivity than previously thought.

Discussion

In an effort to determine the relative chemical activity of atomic fluorine with respect to molecular fluorine, reactions E and F were undertaken. The two reactions were carried out under as near identical conditions as possible except for the fact that in reaction E atomic fluorine was used and in reaction F molecular fluorine was used. Since the atomic fluorine was generated by passing molecular fluorine through a radio-frequency discharge, it was a relatively simple matter to perform experiments with and without the radio-frequency activation. In Table I it can be seen that in reaction E (where atomic fluorine was used) the yield was 28.3% monofluorinated product, while in reaction F (where molecular fluorine was used) the yield was less than 1% monofluorinated product. The use of atomic fluorine increased the percent of monofluorinated product(s) and greatly reduced polymer formation.

Figure 1 related the fluorine to substrate ratio to the recognizable fluorinated products. As the ratio was increased in the experiment, the percent recognizable product also increased.

If the original attack of the benzotrifluoride occurs as shown below, the benzotrifluoride radical produced can react in three ways: (1) with atomic fluorine to produce monofluorobenzotrifluoride; (2) with another benzotrifluoride radical to produce bis(trifluoromethyl)biphenyl; (3) with a benzotrifluoride molecule to initiate polymerization.



Increasing the availability of the fluorine atoms with respect to benzotrifluoride radicals increases the amount of monofluorinated products and decreases the amount of polymer formed. Figure 1 shows this relationship.

In earlier atomic fluorine work Vasek and Sams[7] reported finding greater selectivity than would have been pictured from literature discussions of free-radical reactions. The findings of this study show a definite relationship between the fluorine to substrate ratio and isomer distribution. The ortho and meta

Table I. Reaction Conditions and Yields

Reaction	Fluorine / benzotrifluoride	Fluorine mmol	Benzotrifluoride, mmol	Reaction time, h	Monofluorobenzotrifluoride / reactant benzotrifluoride (100)	Isomer of monobenzotrifluoride / benzotrifluoride (100)		
						Ortho	Meta	Para
A	0.918	25.82	28.11	3	1.63	0.694	0.242	0.694
B	1.56	25.82	16.58	3	1.98	0.302	1.01	0.669
C	3.91	25.82	6.57	3	3.62	0.301	1.36	1.96
D	10.7	59.02	5.54	4	17.2	0	0	17.2
E	15.8	59.02	3.74	4	28.3	0	0	28.3
F	15.7	29.51	1.58	2	0.836	0.356	0.477	0.00211

[a] All reactions were with atomic fluorine, except F, which was with molecular fluorine.

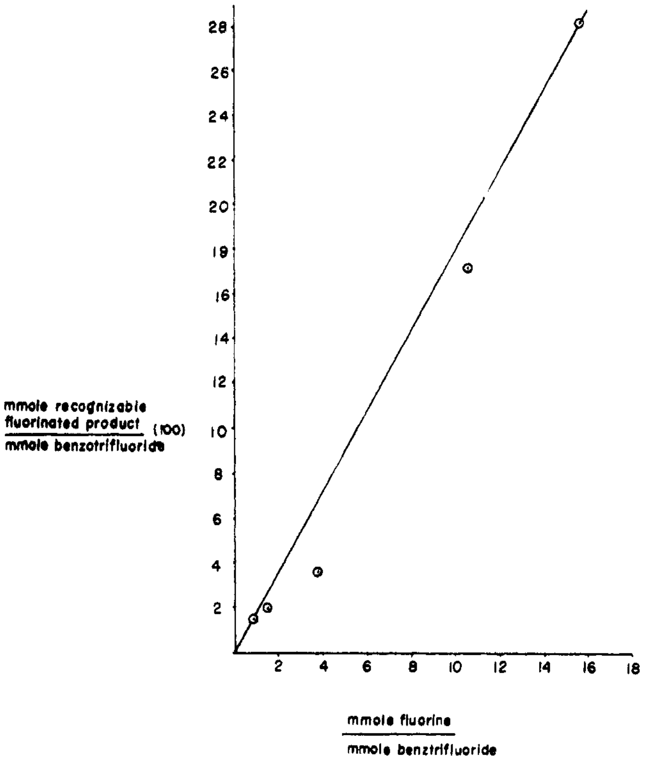


Figure 1.

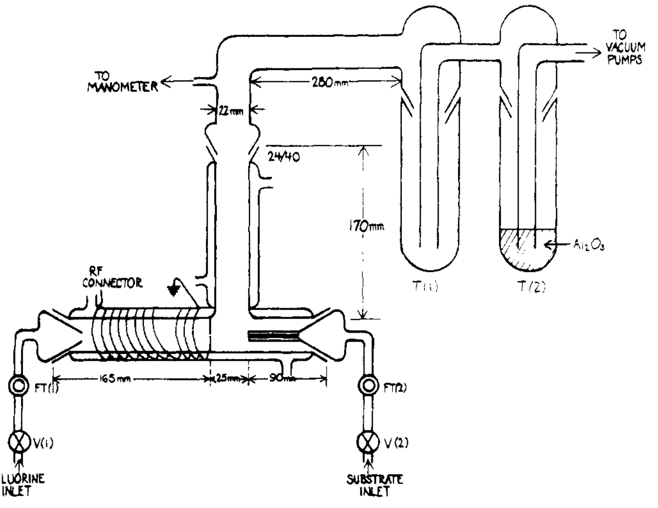


Figure 2.

isomers are only produced when the fluorine to substrate ratio is less than 10.7, while above this point only the para isomer is produced. The question has arisen as to why only the para isomer was found above the fluorine to substrate ratio of 10.7. One possibility was that the ortho and meta isomers were not stable under the conditions of the reaction and may have been converted to the para isomer. In order to answer this question, several reactions were carried out under identical conditions as before except that the ortho isomer and the meta isomer were consecutively used as substrates. Following the reaction the products were analyzed as before. No para isomer was found in either product. These data show that under the conditions of the reactions the ortho and meta isomers are stable and rule out the possibility of isomer interconversion. From Table I it is evident that the para isomer production is proportional to the increasing ratio. Unlike the ortho and meta isomers, the para isomer continued to increase in a somewhat linear fashion up to the limits of experimental capability.

Since this study reports remarkable isomer specificity, a discussion is called for. When the fluorine to benzotrifluoride ratio is above 10.7, the para isomer is the exclusive product. One explanation, as stated earlier, is that under these conditions the ortho and meta isomers are first formed and then converted to the para isomer. This hypothesis, however, has been discounted because the ortho and meta isomers have been found to be stable under the conditions of the reaction.

A second explanation seems indicated from previous work. While studying the reaction between fluorobenzene and atomic fluorine, Vasek and Sams[7] found that the ortho and para fluoro isomers predominated. One would expect to find that the trifluoromethyl group would also be very electronegative and direct into the ortho and para positions. The trifluoromethyl group is much larger in size than the fluoro group and it can be shown to sterically hinder the ortho position. Considering the above, it follows that the reaction products would be almost entirely para.

Experimental Section

Materials. Benzotrifluoride was obtained from PCR, Inc. *o*-Fluorobenzotrifluoride, *m*-fluorobenzotrifluoride, and *p*-fluorobenzotrifluoride were purchased from Pierce Chemical Co. After the infrared spectra checked with the literature,[8] the compounds were used as received.

A new reactor using the molecular beam design was constructed of Pyrex glass according to Figure 2. The reactor was activated inductively with a radio-frequency generator (Johnson Viking Model II) with deliverable power from minimum up to 180 W. The experimental setup contained a Johnson Viking impedence matching box. All experiments were carried out at a radio frequency of 29.1 MHz.

The fluorine gas and benzotrifluoride vapor used throughout were measured by means of Hasting Mass Flowmeters Model LF-20 which were equipped with Monel metal fittings. The flow rates of both gases were regulated with Hoke fine metering valves V(1) and V(2).

The reaction products were analyzed by gas chromatography using a Benton-34 column in a fashion similar to that previously described by Seiler, Durrance, and Sams.[9] The quantity of each isomer was determined by comparison of peak areas to that of calibration curves derived from authentic compounds. Product isomers were identified by comparison of their infrared spectra to that of the authentic compounds.

The light emitting from the fluorine plasma glow discharge has been analyzed during a reaction using a Welch No. 3690A spectrometer with a 600-mm grating and the following wavelengths were observed: 6242, 6353, 6412, 6908, and 6862 Å. These values are consistent with those reported for atomic fluorine by Stringanov and Sventitskii.[10] This laboratory found the shorter wavelength lines to be the most intense while Stringanov and Sventitskii reported the longer wavelength lines to be the most intense. This should be expected since our lines were measured on light coming from a high-energy plasma discharge and their lines were measured on light coming from a low-energy arc discharge. Realizing that it would have been very helpful to know the exact percentage of atomic fluorine passing from our plasma generator, a careful survey of the literature has been undertaken. Rosner and Allendorf[11] endeavored to determine atomic fluorine concentrations in several different ways. They included in their methods chemiluminescent titration reactions and calorimetric probes. In the chemiluminescent titration reactions using NOCl the simultaneous presence of molecular fluorine seriously complicates the determination, since molecular fluorine is able to react with NO to form NOF as well as atomic fluorine. Although Rosner and Allendorf studied calorimetrically the reactions of atomic fluorine with many different metals, their data regarding atomic fluorine concentration resulted only in qualitative estimates. In an effort to gain quantitative data regarding the output of the atomic fluorine generator used, our group undertook a study involving the reaction between silver mirrors and atomic fluorine which resulted again only in qualitative information. The best information regarding atomic fluorine concentration has come from the relative intensity of the atomic fluorine emission lines known to originate from atomic fluorine.[10]

In Table I reactions A–E were carried out in a manner as indicated below. The fluorine and benzotrifluoride flow rates were established in a manner necessary to give increasing fluorine to benzotrifluoride ratios.

In a typical reaction undiluted elemental fluorine was passed through metering valve V(1) and flow transducer FT(1) into the previously evacuated reactor which was cooled by condensers maintained at 0 °C. The fluorine was then allowed to pass into the discharge region where the red glow characteristic of atomic fluorine[12] was initiated by the radio-frequency field. A beam of fluorine atoms then passed into the reaction chamber by way of a 0.75-mm hole in a glass septum, as shown in Figure 2. The temperature of the beam of fluorine atoms was measured after passing through the 0.75-mm hole and was found to be 14 °C. Following the stabilization of the fluorine flow, benzotrifluoride vapor was introduced by placing the substrate in a small flask, maintained at 25 °C, and allowing the autogenous vapor pressure (≃23 Torr) to cause a flow through metering valve V(2), flow transducer FT(2), and then into the reaction chamber through the 0.75-mm i.d. capillary tube. The flow carried the products from the reaction chamber and they were condensed in trap T(1) which was cooled by liquid nitrogen.

At completion of the reaction the contents of trap T(1) were removed and analyzed according to Seiler.[9]

Registry No.—Atomic fluorine, 14762-94-8; benzotrifluoride, 98-08-8.

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The Apparent Oxidation of Triphenylmethane by Triflic Acid[1]

Steven S. Kantner and Maurice M. Kreevoy*

Chemical Dynamics Laboratory of the University of Minnesota, Minneapolis, Minnesota 55455

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The apparent oxidation of triphenylmethane to triphenylcarbonium ion by triflic acid is shown to be the result of dealkylation of one of the benzene rings followed by hydride transfer from unreacted triphenylmethane to the diphenylcarbonium ion, a disproportionation rather than an oxidation. Some other apparent oxidations in strong acid solvents may be similar. Triflic acid is a convenient solvent in which to study the chemistry of stabilized carbonium ions.

The apparent abstraction of hydride ion from hydrocarbons by Lewis and/or Brønsted acids is a well-known process.[2–5] Three mechanisms have been demonstrated.[4] The purpose of this paper is to demonstrate a fourth mechanism and to show that trifluoromethanesulfonic acid (triflic acid) is a convenient solvent for such reactions.

Results

Treatment of triphenylmethane with about ten times its own weight of triflic acid gave about a 50% yield of the triphenylcarbonium ion, a 76% yield of benzene, and a 22% yield of diphenylmethane, as judged by the visible (Figure 1) and NMR spectrum of the reaction mixture and the products obtained after quenching with aqueous base. A 0.1% yield of antracene was also formed. No gas is produced or consumed in this reaction.

On the other hand, a dilute solution of triphenylmethane in triflic acid (7×10^{-3} M) gave an essentially quantitative yield of diphenylcarbonium ion, as judged by its visible spectrum (Figure 2). At intermediate concentrations intermediate results were obtained, as shown in Table I.

Diphenylmethane was not completely soluble in ten times its own weight of triflic acid. After stirring for 1 h at room temperature and quenching, the steam distillate was mostly starting material but also contained 0.8% yield of anthracene, which dominated its visible and UV spectrum because of its spectral intensity (Figure 3).

For comparison purposes the visible and UV spectroscopic behavior of a number of aromatic hydrocarbons and ions was examined in triflic acid. Benzene gave essentially the same spectrum as in cyclohexane. Toluene gave an additional broad band centering around 320 nm. The apparent extinction