Substrate Selectivity and Orientation in Aromatic Substitution by Molecular Fluorine

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Abstract: Direct elemental fluorination of representative aromatic substrates, including PhH, $PhCH_3$, PhF, PhCl, PhBr, $PhNO_2$, PhCN, and $PhOCH_3$, has been investigated in inert solvents, e.g., CCl_3F and other fluorocarbons, over the temperature range −154 to 40 °C. In order to achieve the necessary control of the extremely reactive electrophile, and to minimize unwanted modifications of the reaction environment, the fluorination has been carried out at extremely low rates and correspondingly low conversions, generally below 0.01%, using as a reagent gaseous mixtures of F_2 highly diluted (<1 mol %) in N_2 or Ar. The partial rate factors, calculated from a consistent set of relative reactivity and orientation data measured at −78 °C in CCl_3F, correlate smoothly with the σ^+ constants for all the substituents investigated, giving a ρ^+ value of −2.45 for aromatic substitution by elemental fluorine with a correlation coefficient of 0.993. These results characterize F_2 as a highly reactive, and correspondently unselective, reagent, and support a polar electrophilic substitution mechanism that is discussed and compared with other plausible fluorination pathways.

Direct elemental fluorination of aromatic compounds has remained an unsolved problem for decades, and since Moissan's early attempts[3] there have been very few reports[4] of preparative procedures based on the use of F_2.

A long history of explosions, formation of tars, and uncontrollable reactions has completely discouraged systematic approaches to aromatic substitution by elemental fluorine, despite advances in the experimental techniques and theoretical interest[5,6] in this subject.

In a preliminary communication we have reported the first data on substrate selectivity and orientation in direct elemental fluorination of a few representative aromatic substrates, i.e., toluene, anisole, and nitrobenzene, carried out in inert solvents at low temperatures.[7]

The purpose of this paper is to report the extension of this investigation to a number of other substrates, and to suggest a mechanistic picture of liquid-phase aromatic substitution by elemental fluorine.

Outline of the Experimental Approach. A brief account of the specific problems associated with the use of F_2 as an electrophilic reagent is useful for a discussion of the results. In the first place, the almost complete lack of solubility of elemental fluorine in the relatively few solvents, mostly fluorocarbons, that are sufficiently unreactive toward the halogen prevents application of conventional kinetic techniques, in that no F_2 solutions of known concentration can be prepared and stored. Furthermore, low F_2 solubility makes "liquid-phase" fluorination an essentially "heterogeneous" process, occurring at the gas–liquid interface when the gaseous reagent is bubbled through the substrate solution. Under such conditions, the unique properties of elemental fluorine, that set it apart from other halogens, in particular (1) the high reactivity, (2) the exceptionally high heat of reaction, (3) the low dissociation energy of F_2, and (4) the formation of a highly reactive and corrosive product such as HF, confer on F_2 an extraordinary ability to cause profound *local* modification of the reaction environment. Thus, the low thermal capacity, heat transfer, and mixing rate of gas–liquid reaction interface cause a *local* increase of temperature that in turn can promote F_2 dissociation and chain reaction, further fluorination of primary substitution products, and extensive *local* changes in the nature and the polarity of the solvent, particularly undesirable in mechanistic studies. In view of these difficulties the only viable approach is a competition method comparing the *initial* fluorination rate of two aromatic substrates at "infinite" F_2 dilution and nearly zero conversion.

To this end, the fluorination was carried out in the dark, at low temperature, typically −78 °C, in inert solvents such as CCl_3F, using as a reagent a highly dilute (<1 mol %) F_2/N_2 mixture, at a low $[F_2]$:[substrate] ratio. The fluorination rate was extremely slow, typically in the range of 10^{-9} mol L^{-1} s^{-1}, which corresponded to conversions of ca. 0.01%, approaching the limit of analytical sensitivity. The application of such low-temperature fluorination procedures, and the associated techniques for the preparation and handling of diluted F_2 solutions, was aided by the experience accumulated in the past few years from the synthesis of ^{18}F-labeled radiopharmaceuticals by direct elemental fluorination.[8]

Experimental Section

Fluorination. Standardization of F_2–N_2 Mixtures. Fluorination mixtures were prepared and titrated on the same day that the fluorinations were carried out. Typically, 0.33 mmol of F_2 (Matheson Co., 98.5% purity) was measured utilizing an all-nickel vacuum line and a special nickel chamber pressure transducer (Datametrics). The HF had been removed by passing the tank F_2 through a Matheson Co. NaF trap.

The F_2 was diluted with N_2 gas (99.999 mol %, research grade, Airco) to a total volume of 426 mL at 2.50 atm and 25 °C, corresponding to 977 mL STP (43.6 mmol). The calculated mole fraction of F_2 in the mixture is therefore 0.76%. The iodometric titration of aliquots of the gaseous mixture gave 0.71 ± 0.05 mol % (average of three runs). Research-grade organic may also be used.

It should be emphasized that handling pure F_2, as required for the preparation of the fluorination mixture, requires major safety precautions, including use of all-nickel transfer and vacuum lines, explosion shields, and thorough removal of any kind of organic contaminants from all tubing containing fluorine gas.

Recently, diluted F_2 solutions in inert gases (N_2, Ne, or Ar) have become commercially available, and their use is considerably safer. Nevertheless, in our experience commercial mixtures appear less suitable for mechanistic studies, providing less consistent results than mixtures prepared just before use by carefully mixing measured volumes of the components by standard vacuum techniques. In fact, the concentration of F_2 in commercial mixtures, especially those that are highly dilute, shows large deviations from the nominal value and their relatively long storage in the cylinders affects the purity of the reagent as well. These deviations can also result from organic materials which can be found in the N_2 gas which react with the F_2 which is added. This can be avoided by using research-grade nitrogen or by scrubbing the nitrogen before adding the F_2. It should also be noted that commercial F_2 contains traces of fluorocarbons, predominantly CF_4. The use of an electrolysis cell should be considered if ultra-high-purity F_2 is required. Fluorinations were effected by slowly bubbling the gas mixture through a dilute (0.01–0.1 M) solution of the aromatic substrate(s) in inert solvents (CCl_3F, C_6F_6, C_7F_8, CH_2F_2, or CH_3CN), maintained in the dark at low temperature in a cooling bath, and

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Table I. Reactivity Relative to Benzene and Orientation in Direct Elemental Fluorination in CCl_3F at −78 °C

substituent (X)	$k_{C_6H_5X}:k_{C_6H_6}$	isomeric composition of C_6H_4XF, % ortho	meta	para
CH_3	4.7 ± 0.05	60 ± 2	11 ± 1.5	29 ± 2
CN	0.022 ± 0.004	27 ± 3	62 ± 5	13 ± 2
NO_2	0.017 ± 0.004	9 ± 2	80 ± 3	11 ± 2
CF_3	0.030 ± 0.005	16 ± 2	64 ± 4	20 ± 2
OCH_3	54 ± 2	76 ± 3	0.5 ± 0.1	23.5 ± 2
Br	0.12 ± 0.02	23 ± 2	17 ± 2	60 ± 4
Cl	0.16 ± 0.02	40 ± 3	16 ± 2	46 ± 4
F	0.40 ± 0.1	22 ± 2	13 ± 2	65 ± 5

previously deoxygenated with dry N_2. The all-glass reaction vessel was similar to that described in a previous report.[8a] The purity of the solvents and the substrates had been previously determined by GLC on the same columns used for the analysis of the reaction products. After the fluorination, the cold reaction mixture was thoroughly outgassed with dry N_2 and allowed to come to room temperature for the gas chromatographic analysis.

Product Analysis. The products were analyzed by GLC using either a Perkin-Elmer 900 or a Hewlett-Packard Model 5700 equipped with FI detectors.

The products were identified by comparison of their retention values with those of authentic samples, obtained from Aldrich Co., K & K Laboratories, Inc., and PCR Chemicals, Inc. In many cases the identification was confirmed by GLC–MS, using a Hewlett-Packard Model 5986-A mass spectrometer, operated in the EI or CI mode. The relative yields of the products were deduced from the areas of corresponding elution peaks, corrected for the different FID response to the various fluorinated compounds using individually determined calibration factors.

The capillary columns A (Carbowax 20M, WCOT, 150 ft), B (Carbowax 20M, SCOT, 100 ft), C (OV-17, WCOT, 150 ft), D (squalane, WCOT, 150 ft), E (DEGS, SCOT, 100 ft), F (silicone oil DC 702, WCOT, 300 ft), or their combinations were used for the separation of the products from the different substrates, both neat and in competition with benzene, as summarized below: $PhCH_3$, columns A + C at 50 °C, columns A + B at 68 °C, or columns A + B + E at 75 °C; $PhCF_3$, column C at 70 °C; $PhOCH_3$, columns B + C at 80 °C or columns B + E at 90 °C; PhCN, column B at 110 °C; $PhNO_2$, column B at 130 °C or columns A + B at 130 °C; PhCl, column D at 35 °C, until the elution of PhF, then at 60 °C; PhF, four columns D at 63 °C or columns B + D + two columns E at 65 °C; PhBr, columns C + F at 65 °C. For the analysis of $PhCH_2F$ from toluene columns A + B were operated isothermally at 75 °C, until fluorotoluenes were eluted, then at 130 °C. In addition, a 2-m SE-30 column was used at 300 °C and high flow rates to detect any high-boiling or relatively unvolatile products from the fluorination of toluene.

Fluorination of Bromobenzene. The experimental method described below is typical for the fluorinations. Bromobenzene (1.00 mL, 9.94 mmol) (previously analyzed by GLC) was dissolved in CCl_3F to an approximate volume of 50 mL or ~0.2 M in C_6H_5Br, cooled to −78 °C, and fluorinated in the dark. Dry nitrogen (~100 mL) was first passed through the solution followed by 35.0 mL of the F_2/N_2 mixture, measured at 25 °C and atmospheric pressure. This corresponds to 0.0108 (manometric) or ~0.0100 mmol of F_2 (based on the titration).

The solution was protected from moisture by a $CaCl_2$ trap. The fluorination time was 1 h. The solution was effectively stirred by the bubbles of the N_2/F_2 mixture flowing from a very thin Teflon outlet tube. Under the conditions employed, no F_2 escaped from the vessel, as could be demonstrated utilizing KI-starch paper. The maximum conversion of the substrate was 10^{-3} = 0.0100 mmol F_2/10 mmol C_6H_5Br. After the end of the fluorination, 100 mL of dry, pure N_2 was passed through the solution to sweep out any HF or other gaseous fluorinated products. The mixture was allowed to come to room temperature for the GLC analysis.

GLC Analysis of Bromobenzene. Preliminary experiments were carried out to show that all relevant compounds could be separated using a composite column, formed by joining a 150 ft DV-17 coated stainless steel capillary column to a 300 ft DC 702 coated stainless steel column, operated at 65 °C, at an inlet pressure of 5.5 atm. Under these conditions, the retention times were as follows: (a) *m*-fluorobromobenzene, 18.25 min; (b) *p*-fluorobromobenzene, 20.01 min; (c) bromobenzene, 21.50 min; (d) *o*-fluorobromobenzene, 24.50 min. Owing to the good resolution and the narrow peaks obtained, it was possible to work in the splitless mode, injecting relatively large amounts of sample. Calibration experiments (carried out with a test mixture containing 1.560 g of *o*-fluorobromobenzene, 1.485 g of *m*-fluorobromobenzene, 1.660 g of *p*-fluorobromobenzene, and 1.250 g of bromobenzene) indicated that the response of the FI detector to the various compounds relative to bromobenzene was 0.96 ± 0.02 for all fluorobromobenzenes.

A relatively large volume of the reaction mixture (corresponding to 1.0 μL of bromobenzene) was injected into the columns in the splitless mode. The peak of C_6H_5Br was badly shaped, owing to the severe overloading of the column; nevertheless, the analysis of the products is facile. The *o*-bromofluorobenzene peak came out on the tail of the large C_6H_5Br peak, but owing to the very sharp line-shape integration was readily accomplished. The attenuation was set at *×1600 for C_6H_5Br and at ×2 for its fluorinated products.*

A confirmatory test was carried out using a SCOT stainless steel capillary column (200 ft, Carbowax 20M, 75 °C, 3 atm inlet pressure) that gave a good separation of all the products of interest, except the bromobenzene/*p*-fluorobromobenzene pair. The results with this column were consistent (within about 10%) with those obtained with the other columns.

The procedure described is typical for conversions of ~0.1%. For lower conversions, and for GLC/MS analyses, the "peak cutting" technique was used, based on the use of a preliminary column (generally a short SCOT column) followed by a zero-volume high-temperature VALCO switching valve.

Immediately after elution of the large peak of the unreacted substrate, the effluents from the preliminary column were directed into a SCOT analytical column (flushed up to that moment by an auxiliary carrier gas stream). The outlet of the analytical column was connected (with the same valve operation) to the FID detector or to the ion source of the mass spectrometer. The "peak cutting" technique has proven to be particularly useful in these analyses, extending their sensitivity and allowing one to reduce the conversion of substrate as noted. The technique is described by Deans.[8b]

Results

Relative Reactivity and Orientation. The reactivity relative to benzene and the isomeric composition of ring-substituted products from the fluorination of typical aromatic substrates in CCl_3F at −78 °C are given in Table I. The data listed are the mean values of the results obtained from separate reactions where the relative concentrations of the competing substrates were systematically changed over a range that covered, for the $PhH/PhCH_3$ pair, almost three orders of magnitude. In all cases such changes in relative concentrations failed to significantly affect the ratio of rate constants, consistent with a first-order dependence of the fluorination rate on the substrate concentration.

The partial rate factors, calculated from the data of Table I, are given in Table II and plotted in Figure 1 *vs.* the appropriate σ^+ constants for the substituents investigated, showing a smooth linear dependence with a ρ^+ value of −2.45 and a correlation coefficient of 0.993.

Effects of the Nature of the Solvent and the Temperature on the Relative Reactivity and Orientation. The results of a systematic study on the $PhH/PhCH_3$ pair are illustrated in Table III. It is apparent that both the substrate and positional selectivity increase, in a given solvent, as the temperature is decreased. Thus, in CCl_3F the k_T/k_B ratio increases from 4.2 ± 0.3 at 0 °C to 4.70 ± 0.05 at −78 °C to 5.2 ± 0.2 at −97 °C, with a parallel enhancement of the para:meta ratio. Furthermore, at a given temperature, the selectivity appears to decrease when the reaction is carried out in a more polar solvent, such as CH_3CN.

However, the results obtained in acetonitrile must be taken with some reservation. In fact, despite the lack of evidence for reactions of F_2 with CH_3CN and the use of the latter as a solvent in preparative fluorination of aromatics,[4] acetonitrile

Table II. Partial Rate Factors for Direct Elemental Fluorination in CCl_3F, −78 °C

substituent (X)	m_f^X	p_f^X
CH_3	1.55	8.2
CN	0.041	0.017
NO_2	0.041	0.011
CF_3	0.058	0.036
OCH_3	0.81	76.1
Br	0.061	0.43
Cl	0.077	0.44
F	0.16	1.56

is known[4,10,11] to undergo fluorination (usually under conditions more drastic than those prevailing in the present study), giving fluoroacetonitrile and other products that could conceivably interfere with direct atomatic substitution.

Attack on the Substituent Group and Other Reaction Channels. The product pattern emerging from the gas chromatographic analysis of the products has shown that under the reaction conditions prevailing in the present study the substitution is a major, and frequently the only detectable, channel, with the following notable exceptions.

Iodobenzene gives no iodofluorobenzene at all, the only product observed being a trace of yellow material at the outlet of the F_2/N_2 adduction tube. Bromobenzene undergoes limited fluorodebromination giving PhF, whose yield amounts to 15% of the combined yields of bromofluorobenzenes in CCl_3F at −78 °C.

In addition to the fluorotoluenes, $PhCH_3$ gives benzyl fluoride, whose yield depends markedly on the temperature and rate of fluorination. Thus, in CCl_3F solution the yield of $PhCH_2F$ passes from less than 10% of the combined yields of fluorotoluenes at −97 °C to ca. 20% at −78 °C and to ca. 50% at 0 °C. These data refer to fluorination carried out at extremely low (<0.1%) conversions, while substantially higher yields of benzyl fluoride can be expected at higher temperatures, or at higher conversion rates as prevail in preparative procedures. From the extreme and indiscriminate reactivity of F_2 a variety of processes can be expected in addition to ring substitution, and indeed fragmentation products, polymers, unstable unsaturated compounds, or highly fluorinated cyclohexane derivatives have been observed in preparative methods involving elemental fluorine.[12]

High-temperature GLC of crude reaction mixtures from the fluorination of PhH and $PhCH_3$ has failed to detect relatively nonvolatile products, such as substituted biphenyls and polyphenyls that would certainly have been eluted from the short SE-30 column at temperatures up to 300 °C and high flow rates used. Nevertheless, the formation of higher polymers or other nonvolatile and/or unstable products cannot be excluded on the grounds of the gas chromatographic results. Another approach to evaluating the relevance of aromatic substitution among the different reactivity channels conceivable for F_2 is obviously to measure the *absolute* yields of ring-substituted products. Unfortunately, the amount of F_2 consumed at the low conversion rates typical of this investigation was too low to allow determination by differential titration with any significant degree of accuracy. However, aromatic substitution is known from investigations carried out at substantially higher conversions to represent a major reaction channel for F_2. As an example, fluorination of nitrobenzene was reported[4c] to give an 89.9% yield of fluoronitrobenzenes at a conversion of 18%, benzoic acid to give a 37.1% yield of fluorobenzoic acids at a conversion of 64.3%, etc. The yields of ring-substituted products can be expected to be even higher at low conversion, following a well-established trend for the F_2 reactivity, both in solution and in the gas phase.[13]

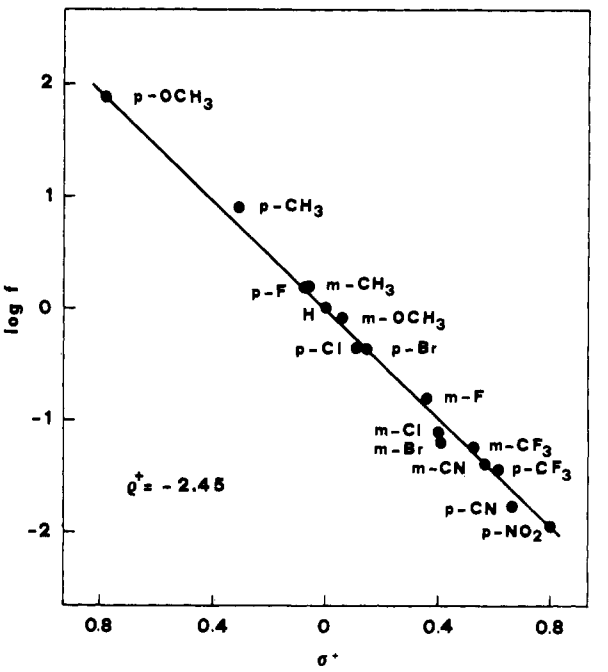


Figure 1. Logarithmic plot of partial rate factors vs. σ^+ constants for elemental fluorination in CCl_3F at −78 °C.

Discussion

Fluorine is characterized by its extreme reactivity toward organic compounds. Even at temperatures as low as 4 K, pure F_2 is known to react with solid alkenes and aromatics, as demonstrated by detection of radicals with ESR techniques.[14] In view of such extreme and indiscriminate reactivity, the attack of elemental fluorine on aromatic substrates could conceivably involve multiple, and possibly overlapping, pathways, and consequently interpretation of the results according to a common mechanistic model requires caution. This is especially true if one considers the limitations of the kinetic and mechanistic tools imposed by the very nature of the reagent, including the restricted choice of solvents, the lack of useful radical scavengers, etc.

Nevertheless, once clearly stated that the discussion is re-

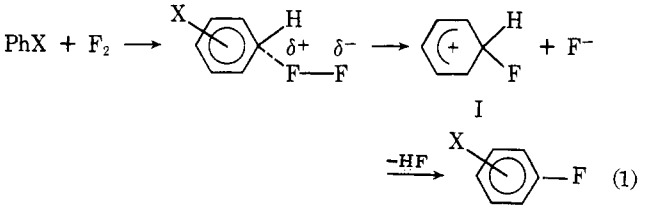
Table III. Effect of Solvent and Reaction Temperature in the Competition of Benzene and Toluene for F_2

solvent	t, °C	$k_T:k_B$	isomeric composition of fluorotoluenes, %		
			ortho	meta	para
C_7F_8	40	2.4 ± 0.3	54 ± 2	17 ± 2	29 ± 2
C_6F_6	0	2.7 ± 0.3	52 ± 3	15 ± 2	33 ± 2
C_7F_8	0	2.8 ± 0.2	56 ± 3	15 ± 2	29 ± 2
CCl_3F	0	4.2 ± 0.3	60 ± 3	13 ± 2	27 ± 2
CH_3CN	−23	3.4 ± 0.4	56 ± 2	14 ± 2	32 ± 2
CCl_3F	−23	4.2 ± 0.3	62 ± 3	11 ± 1	27 ± 2
CCl_3F	−78	4.7 ± 0.05	60 ± 2	11 ± 1.5	29 ± 2
CCl_3F	−97	5.2 ± 0.2	60 ± 3	9 ± 2	31 ± 3
CH_2F_2	−154	5.9 ± 0.3	59 ± 3	7 ± 2	34 ± 3

stricted to ring substitution occurring at low temperature in inert solvents under conditions approaching "zero" conversion and "infinite" F_2 dilution, it is our contention that all experimental results fit neatly into a consistent reactivity pattern characterized by a polar electrophilic mechanism that will be illustrated in the next section.

The remaining part of the paper is devoted to discussion of alternative fluorination routes, and to critical comparison of their features with pertinent experimental results.

Polar Substitution Mechanism. Extension of the investigation to a larger number of substrates has provided strong support for the mechanistic hypothesis suggested in our preliminary report,[7] namely, that ring substitution has polar character, proceeding via the intermediate formation of an arenium ion and a fluorine ion, possibly forming a "contact" ion pair in the aprotic solvent.[15] Such an interpretation is fully

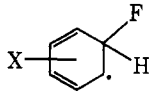


consistent with the relative reactivity and orientation that characterize molecular fluorination as a typically electrophilic, if highly unselective, substitution process.

A quantitative illustration of this view is provided by the excellent logarithmic correlation of the partial rate factors with the σ^+ constants typical of polar aromatic substitution, shown in Figure 1, giving a ρ^+ value of -2.45 and a correlation coefficient of 0.993. Further support is provided by the observation that the data fit the Brown selectivity relationship reasonably well.[16]

If one accepts the mechanism outlined in eq 1, molecular fluorine can be characterized as a very reactive and unselective electrophile, as demonstrated by a comparison of its ρ^+ value, -2.45, with those for elemental chlorination, -10.0, and elemental bromination, -12.1, measured in water/acetic acid at 25 °C.[17] The considerable reactivity difference between F_2 and Cl_2 that greatly exceeds that between Cl_2 and Br_2 is not unexpected, and parallels the unique behavior of elemental fluorine in electrophilic aliphatic substitution.[18,19]

Radical Mechanisms. The remarkably low dissociation energy of F_2 makes radical processes quite common in organofluorine chemistry. Several mechanistic hypotheses based on radical processes will be briefly discussed in this section. Aromatic substitution can involve a fluorocyclohexadienyl



II

intermediate formed either by addition of F atoms[20]

$$F_2 \rightarrow 2F\cdot \quad (2)$$

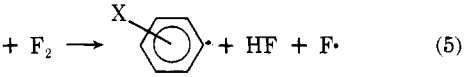
$$F\cdot + PhX \rightarrow II \quad (3)$$

or, more likely, by direct attack of fluorine:

$$F_2 + PhX \rightarrow II + F\cdot \quad (4)$$

The intermediate can subsequently collapse to the observed ring-fluorinated products by a disproportionation reaction with F_2 or via other unspecified channels. The major difficulty with any hypothesis involving the intermediacy of II is that orientation in substrates containing electron-withdrawing groups such as NO_2 or CN should be predominantly ortho/para, as invariably observed in homolytic aromatic substitution,[21-23] and, in particular, convincingly argued in the specific case of aromatic fluorination.[24] Indeed, a distinctive feature of polar aromatic substitution, as opposed to homolytic processes involving intermediates II, is the definite meta orientation in nitrobenzene and acetonitrile, which indeed is observed in elemental fluorination.

Another conceivable radical route involves intermediacy of phenyl radicals formed via hydrogen abstraction processes, e.g., eq 5, followed by reaction with F_2 or recombination with fluorine atoms. This mechanism can be ruled out on the grounds of the results concerning fluorination of toluene, either neat or in competition with benzene. In fact, abstraction of H from the methyl group of toluene is known to be largely favored over H abstraction from the ring.



(5)

Consequently, if ring substitution would proceed exclusively or predominantly via process (5), it should be suppressed in the presence of toluene, contrary to experimental evidence concerning the relative reactivity of $PhCH_3$ vs. PhH and the ratio of nuclear to side-chain fluorination for toluene itself.

Finally, in light of a recent interpretation of aromatic nitration provided by Perrin,[25] one might consider a mechanism involving intermediacy of a radical cation, followed by recombination of the ion pair:

$$PhX + F_2 \rightarrow Ph^+\cdot + F^- + F\cdot \quad (6)$$

However, in contrast with the analogous process promoted by nitronium ion, reaction 6 would be energetically unfavorable. Furthermore, it has been long established that F^- fails to undergo nucleophilic attack on aromatic radical cations,[26,27] a result recently rationalized by a theoretical interpretation offered by Eberson et al.[6]

In conclusion, it appears that all the radical reaction pathways encounter major difficulties in being consistent with the experimental features of the ring-substitution process promoted by molecular fluorine.

Comparison with Previous Results. No relative reactivity data on elemental fluorination of aromatics are currently available. As to orientation, comparison must be restricted to the few data obtained from fluorination carried out under preparative conditions. In particular, from the NMR analysis of the products from the reaction of F_2 with aromatics, either undiluted or in acetonitrile at -70 °C, the following ortho:meta:para ratios have been obtained: 5:1:4 from $PhCH_3$; 1.5:9:1 for $PhNO_2$; 3:1:9 for PhCl.[4a] Once allowance is made for the different reaction conditions and the limitations of quantitative NMR analysis, these data appear in reasonable agreement with ours. The orientation observed in a different set of fluorination experiments[4c] carried out at high conversions (up to 71%) at 0 °C in trifluoroacetic acid, namely, 67% ortho, 15% meta, 18% para from $PhCH_3$, 26% ortho, 61% meta, 13% para from $PhCF_3$, and 18% ortho, 65% meta, and 17% para from $PhNO_2$, is also qualitatively consistent with that observed in the present study. Finally, the fluorodebromination occurring to a limited extent in the reaction of F_2 with PhBr has been previously reported as a comparatively minor channel in the gas-phase reaction of PhBr with F_2 gas excited by a radiofrequency discharge.[28]

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Chemiluminescence in the Reaction of a Sulfurane with Alkyl Hydroperoxides

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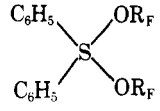
Abstract: The reaction of Martin's sulfurane **1** with *tert*-butyl hydroperoxide, in the presence of 9,10-dibromoanthracene, emits light in two stages. The early stage, beginning on warming to about −40 °C, coincides with the formation of olefin, and is intensified by degassing and quenched by oxygen or by organic sulfides. The later stage, seen on warming from −20 to −10 °C, occurs during the formation of acetone from the hydroperoxide; this luminescence is eliminated by degassing and quenched by 2,6-di-*tert*-butyl-*p*-cresol and organic sulfides. Similar phenomena are observed with cumyl hydroperoxide. Relevant observations are reported on the NMR shifts produced in alcohol proton signals by diphenyl sulfoxide and dimethyl sulfoxide and on the CIDNP signals occurring during the reaction. Some conclusions are drawn concerning the mechanism of the luminescence.

Introduction

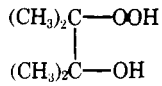
Martin's sulfurane **1** was observed[1] to afford smooth de-



$R_F = -C(CF_3)_2C_6H_5$

1

hydration of 1,2-diols to epoxides and of 1,3-diols to oxetanes. Despite the fact that the sulfurane also reacts with hydrogen peroxide and alkyl hydroperoxides to yield sulfur oxidation products,[2] we hoped that intramolecular dehydration might afford a new route to dioxetanes from the readily available β-hydroxy hydroperoxides such as **2**. In trying the reaction between **1** and **2** in chloroform we found none of the hoped-for



2

$HOOH$ **3**

$(C_6H_5)_3COOH$ **4**

$C_6H_5C(CH_3)_2OOH$ **5**

$(CH_3)_3COOH$ **6**

dehydration to dioxetane, the products being acetone, diphenyl sulfoxide, and R_FOH. (Tetramethyldioxetane, added in a control experiment, underwent no reaction with sulfurane **1**, showing that it could not even have been an intermediate in the acetone formation.) It was noted, however, that the reaction between **1** and **2** in the presence of certain anthracenes was chemiluminescent, and we therefore made some further observations on this previously unreported property of the oxidation of sulfuranes. It was found that there are two distinct luminescent stages in the sulfurane–*tert*-butyl hydroperoxide reaction, associated with the formation of different products and responding oppositely to oxygen. The NMR observation of the stages in the reaction involved distinguishing some important interactions between products and observing a number of dynamic nuclear polarization effects. In this paper we undertake to present these observations in perspective and to indicate what progress has been made and what remains to be done in interpreting the mechanism.

Results

Chemiluminescence was observed in the reaction of **1** with hydrogen peroxide (**3**), triphenylmethyl hydroperoxide (**4**), cumyl hydroperoxide (**5**), and *tert*-butyl hydroperoxide (**6**). The luminescence either requires, or is enormously enhanced

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