unsaturated M^{V} or M^{IV} mononuclear species.

$$\begin{aligned}[M^{VI}O(XR)_4] &\rightarrow [M^{V}O(XR)_3] + SR\cdot \\ &\rightarrow [M^{IV}O(XR)_2] + RSSR\end{aligned}$$

Such processes are certainly the source of the general instability of molybdenum(VI) and tungsten(VI) thiolate species. Stable dioxo–molybdenum(VI) complexes containing multidentate ligands feature[28] trans thiolate–sulfur ligand atoms to suppress disulfide elimination. The EXAFS spectrum[3] of such a complex, $[Mo^{VI}O_2[N(CH_2CH_2S)_2(CH_2CH_2SMe)]$, is intriguingly similar to that of the fully oxidized form of sulfite oxidase.

The importance of thiolate ligand redox processes in the present work is mirrored in significant attractive interactions between cis thiolate ligands in $(Me_4N)_2[Mo^{V}_2O_4(SPh)_4]$[29] and those in $[Mo^{VI}O_2(SC(CH_3)_2CH_2NHCH_3)_2]$.[30] Besides the possibility of such interactions modulating the catalytic properties of molybdenum centers, cysteinate ligand redox processes might be considered in a detailed examination of electron transfer in molybdo enzymes. In the resting II inactive form of xanthine oxidase, electron spin–spin coupling is observed[31] between Mo and Fe_2S_2 which constitutes part of the internal electron-transfer chain. The two centers may be separated by a distance (present estimates[31b] suggest 8–13 Å) which might eliminate a direct low activation energy electron-transfer pathway via Mo and Fe cysteinate ligands. However, involvement of cysteinate ligands (or the recently discovered[32] pteridine unit) would significantly reduce the distance over which electron-transfer mechanisms such as electron channeling or quantum mechanical tunneling would need to operate.

In the present work, the mononuclear–binuclear interconversions appear to be driven by the thermodynamic instability of (a) the metal oxidation state VI relative to V and IV in the presence of the redox-active XR^- ligands, (b) the $M^{V}(d^1)$ mononuclear species relative to M^{V}_2 binuclear species which are certainly stabilized[16] by intermetallic bonding, and (c) the $M^{IV,V}_2$ and M^{IV}_2 binuclear species relative to $M^{IV}(d^2)$ mononuclear species assumed to have low-spin d_{xy}-based ground states (apparently addition of electrons to the spin-coupled species II requires occupation of antibonding levels).

However, examples of mononuclear M^{VI} and M^{V} and binuclear $M^{IV,V}_2$ and M^{IV}_2 are observed as a result of varying degrees of kinetic stability. In this context, $[Mo^{V,IV}_2O_2(SePh)_6(OMe)]^-$ has a significant lifetime at −50 °C in DMF (Figure 4b), and attempts are currently under way to characterize it by ESR spectroscopy.

Acknowledgment. A.G.W. thanks the Australian Research Grants Committee for financial support of this work. J.R.B. acknowledges the award of a Commonwealth Postgraduate Scholarship.

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Reaction of Fluoroxysulfate with Aromatic Compounds[1a]

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Abstract: The fluoroxysulfate ion, SO_4F^-, substitutes fluorine on aromatic compounds in acetonitrile solution at room temperature. However, benzyl fluoride is the principal product from toluene. Other products are also formed, particularly in the case of the less reactive aromatic substrates. Product distributions and relative reactivities are interpreted in terms of an initial electrophilic attack that can be followed by free-radical side reactions.

Introduction

It is rather uncommon to find a reagent that will substitute fluorine for aromatic hydrogen. Molecular fluorine itself tends to add to aromatics,[2,3] although substitution can be achieved under carefully controlled conditions.[3,4] Trifluoromethyl hypofluorite, CF_3OF, only effects clean substitution by means of low-temperature photolysis[5] or in reactions with activated aromatic substrates.[6] Xenon difluoride has been found to produce fluoroaromatics in good yield in the presence of HF as a catalyst,[7] but it is an inherently costly reagent. A very recent publication reports fluorination of aromatics by AgF_2.[8]

The fluoroxysulfate ion, SO_4F^-, has recently been prepared in our laboratory.[9] It is the first ionic hypofluorite to be isolated, and our preliminary results suggested that it might, in fact, react with aromatic compounds as an electrophilic fluorinating agent. Unlike many powerful fluorinating agents, the cesium and rubidium fluoroxysulfate salts are relatively stable compounds that are easy to prepare, store, and use. Because of this, they could have potential application as synthetic reagents for organic chemistry. We have therefore undertaken to study in some detail the reactions of fluoroxysulfate with a variety of aromatic species.

Acetonitrile was found to be a suitable solvent for these reactions. Cesium and rubidium fluoroxysulfates are soluble in

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[1] (a) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy. (b) Undergraduate Research Participant, 1979, supported by the Argonne Center for Educational Affairs.

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CH_3CN to the extent of about 0.07 and 0.12 M, respectively, at room temperature, and the solutions are stable over the course of a working day. Over several days, however, or upon heating of the solution, extensive and somewhat unpredictable reaction takes place, which limits the usefulness of this solvent system for the examination of very slow reactions. We shall also see that some substrates may actually induce reaction between fluoroxysulfate and acetonitrile. Nevertheless, it appears at this time that acetonitrile is probably the most convenient medium in which to carry out reactions of fluoroxysulfate with organic compounds.[10]

Experimental Section

Materials. Cesium and rubidium fluoroxysulfates were prepared by the reaction of fluorine with aqueous solutions of the corresponding sulfates.[9] The 2–5 g batches were made routinely and were stored at −10 °C when not in use.

The following commercial products were used as received: phenol and methyl benzoate (Aldrich 99%); anisole, benzonitrile, biphenyl, and 1,3,5-trinitrobenzene (Eastman); benzene and toluene (AMAR Analytical Reagent Grade); fluorobenzene (Pierce Chemical Co.); nitrobenzene (Sargent-Welch, Purified Grade); and naphthalene (Baker Analyzed Reagent).

Acetonitrile (Mallinckrodt SpectrAR) was stored over 3A molecular sieves (activated at 320 °C) prior to use. For some experiments the acetonitrile was further purified by procedure B of Walter and Ramaley.[11]

Certain experiments were carried out with high purity benzene and toluene (Phillips Research Grade or BDH "Aristar"), phenol (BDH Special for Chromatography), and nitrobenzene (Eastman Electronic Grade). Redistilled anisole was also used in some experiments. Except in the case of the kinetic measurements with toluene (vide infra), results were not sensitive to the source of the chemicals used nor were they affected by the use of repurified materials.

Analytical Methods. Some reaction product mixtures were analyzed by high-pressure LC on a Waters Associates ALC/GPC 201 liquid chromatograph equipped with a Model 660 solvent programmer, a Schoeffel SF770 variable-wavelength spectrometer, and a μ-Bondapak C_{18} 4 mm i.d. × 30 cm reverse-phase column. Solvents employed were various binary or ternary mixtures of acetonitrile, methanol, water, and acetic acid. Flow rate was maintained at 1 mL/min, and a fixed wavelength of 254 nm was used in all runs. Calibration curves were constructed by using authentic samples. At least three runs were made for each analysis; results were reproducible to ±0.5%.

Gas chromatography was carried out on a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector. Two different columns were used, depending on the experiment: column A, 100–120 mesh, 6 ft × 0.085 in. i.d. SS Ultra-Bond Carbowax 20 M column; or column B, 45 M × 0.55 mm i.d. glass SCOT column coated with OV 101. Analysis was performed at a He flow of 37 mL/min on the Ultra-Bond or 3.5 mL/min on the SCOT column under isothermal or temperature-programming conditions. Whenever possible, calibrations were carried out with authentic samples under similar conditions.

GCMS was carried out on a Perkin-Elmer Model 270 system operating at 50-eV electron energy. Solid-probe mass spectra were taken on a Finnigan Model 400 quadrupole spectrometer, and high-resolution mass spectra were taken on an AEI MS902. A Consolidated Model 21-620 mass spectrometer was used for gas analysis.

^{19}F NMR measurements were made in ca. 1:1 CH_3CN/CD_3CN on a Bruker WP 60 spectrometer operating at 56.44 mHz with quadrature detection, using $CFCl_3$ and a measured quantity of an authentic fluoroaromatic compound as internal standards. Authentic reference samples were used whenever possible.

Fluoroxysulfate solutions in acetonitrile were analyzed by reaction with iodide followed by titration with standardized thiosulfate. The peroxydisulfate content of solutions was determined by adding an aliquot to a 1 M KI solution, saturating with N_2, and allowing the iodide solution to stand for 15 min before titrating with thiosulfate. The difference between the titer obtained in this way and that resulting from prompt titration in 0.1–0.2 M KI was taken to represent the concentration of $S_2O_8{}^{2-}$.[12]

General Procedure. A saturated solution of $CsSO_4F$ in acetonitrile (ca. 0.07 M) was prepared at room temperature (20–25 °C) and analyzed iodometrically. A portion of this solution was mixed with substrate in a glass vial with a Teflon-lined screw cap. The reaction vial was kept in the dark at room temperature under an N_2 blanket, and the course of the reaction was monitored by periodic iodometric titration. After reaction was complete (usually less than 1% of the SO_4F^- oxidizing power left), precipitated salts were removed by centrifugation, and the supernatant solution was analyzed by high-pressure LC, GC, GCMS, solid-probe MS, or ^{19}F NMR. Yields of fluorinated products obtained by chromatographic methods were verified by ^{19}F NMR, and the NMR results were relied on entirely for fluorinated products formed in very low yields and for the products of reactions in which a large excess of substrate was present. Control experiments showed that reversing the order of mixing did not alter product yields. 1,3,5-trinitrobenzene was added to some reaction mixtures to act as a scavenger of free radicals. Except when specified otherwise, all yields are given as percentages of the fluoroxysulfate initially present.

Phenol. GC (Column A, temperature programmed from 60 to 230 °C at 5 °C/min) showed 71% consumption of phenol and formation of *o*- and *p*-fluorophenol, along with two isomers of difluorophenol (^{19}F NMR signals at 122.4 and 133 ppm). Products were identified by comparison with retention times of authentic compounds and by GCMS. Trace formation of *m*-fluorophenol was suggested by ^{19}F NMR. Production of *p*-benzoquinone was shown by high-pressure LC (CH_3CN/H_2O, 46/54 v/v).

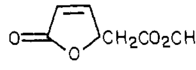
Anisole. GC (Column A, isothermal at 40 °C) showed 67% consumption of anisole and production of *o*- and *p*-fluoroanisole. Formation of *p*-benzoquinone was shown by high-pressure LC ($CH_3OH/H_2O/HOAc$, 58/40/2 v/v/v), which also separated anisole and the fluoroanisoles. Yields from high-pressure LC agreed with those obtained by GC. No *m*-fluoroanisole could be detected by GC, high-pressure LC, or ^{19}F NMR.

Toluene. High-pressure LC (CH_3OH/H_2O, 60/40 v/v) showed 50% consumption of toluene and formation of benzyl fluoride, *o*-fluorotoluene, and *p*-fluorotoluene. No *m*-fluorotoluene, benzyl or fluorobenzyl alcohols, or cresols were detected. GC (column B, temperature initially held at 40 °C for 5 min and then programmed to 230 °C at 5 °C/min) confirmed the yields of benzyl fluoride and *o*-fluorotoluene and indicated the formation of another species that GCMS showed to be either difluorotoluene or fluorobenzyl fluoride. ^{19}F NMR indicated the former (signal only at 137 ppm).[13]

Biphenyl. GC (column B, temperature held at 40 °C for 5 min and then programmed to 230 °C at 5 °C/min) gave peaks corresponding to unreacted biphenyl (35% consumption), 2-fluorobiphenyl, and 4-fluorobiphenyl. ^{19}F NMR of the concentrated, crude reaction mixture confirmed the identity of these products and also showed the presence of 3-fluorobiphenyl. The yield of 4-fluorobiphenyl was determined by ^{19}F NMR because of overlap of its GC peak with that of biphenyl. A number of small NMR signals were also detected (137.8–239.8 ppm), suggesting a complex mixture of other fluorinated products. Mass spectrometric analysis of the crude reaction mixture indicated the presence of tetraphenyl. High-pressure LC did not show any polar products.

Benzene. High-pressure LC ($MeOH/H_2O$, 50/50 v/v) showed 27% consumption of benzene and formation of fluorobenzene and a mixture of polar products. The fluorobenzene yield was not affected when reaction was carried out in CD_3CN or repurified CH_3CN, or in the presence of nitrobenzene, 1,3,5-trinitrobenzene, or hexafluoroisopropyl alcohol. The yield was also unchanged when the reaction was carried out in solutions that had been saturated with N_2 or O_2, nor was it altered by the presence of a tenfold excess of benzene. Biphenyl was not detected as a reaction product.

The reaction mixture was also methylated with dimethyl sulfate/potassium carbonate in anhydrous acetone.[14] GC (column A, temperatue held at 40 °C for 4 min and then programmed to 230 °C at 8 °C/min) showed two major peaks. MS suggested that one of these might be the methylated ring-degradation product[15]



Mass spectrum: *m/e* (relative intensity): 156 (2), 99 (4), 98 (34), 84

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(10) Cesium fluoroxysulfate does not dissolve appreciably in chloroform, methylene chloride, nitrobenzene, *tert*-butyl alcohol, tetrahydrofuran, ethyl acetate, trifluoroacetic anhydride, or hexamethylphosphoramide. Its solubility in nitromethane is about the same as in acetonitrile, but the nitromethane solutions are much less stable. Fluoroxysulfates react violently with dimethyl sulfoxide or dimethylformamide. They dissolve in trifluoroacetic acid with rapid reaction to form the peroxyacid.

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Table I. Kinetics of Reaction of Aromatic Compounds with Fluoroxysulfate in Acetonitrile[a]

substrate	range of initial concn, M: substrate	range of initial concn, M: SO_4F^-	empirical rate law $-d[SO_4F^-]/dt$	rate constant
phenol	0.04[b]	0.009[b]	$k[SO_4F^-][C_6H_6O]$	0.34 M^{-1} s^{-1}
anisole	0.05–0.3[c]	0.009–0.019[c]	$k[SO_4F^-]^{3/2}[C_7H_8O]$	0.55 $M^{-3/2}$ s^{-1}
toluene	0.09–0.66	0.017–0.07	$k[SO_4F^-]^{3/2}[C_7H_8]^{3/2}$	0.15 M^{-2} s^{-1} [d]
			$k[SO_4F^-]^2[C_7H_8]^{3/2}$	1.2 $M^{-5/2}$ s^{-1} [e]
biphenyl	0.08–0.68	0.012–0.03	$k[SO_4F^-]^{3/2}[C_{12}H_{10}]$	0.033 $M^{-3/2}$ s^{-1}
benzene	0.43–2.25	0.016–0.07	$k[SO_4F^-]^{3/2}[C_6H_6]$	0.0029 $M^{-3/2}$ s^{-1}
fluorobenzene	0.4–2.1	0.013–0.062	$k[SO_4F^-]^{3/2}[C_6H_5F]$	0.0016 $M^{-3/2}$ s^{-1}
methyl benzoate	1–2.3	0.013–0.055	$k[SO_4F^-]^{3/2}[C_8H_8O_2]$	5×10^{-4} $M^{-3/2}$ s^{-1}
benzonitrile	1–1.6[f]	0.06–0.11	$k[SO_4F^-]^{3/2}[C_6H_5CN]$	2×10^{-4} $M^{-3/2}$ s^{-1}
nitrobenzene	1–1.6	0.06–0.11	$k[SO_4F^-]^{3/2}[C_6H_5NO_2]$	8×10^{-5} $M^{-3/2}$ s^{-1} [g]

[a] At 25.0 °C. [b] Empirical rate law verified at 0 °C over a range of initial phenol concentrations from 0.04 to 0.14 M and over a range of initial SO_4F^- concentrations from 0.008 to 0.024 M. [c] Empirical rate law verified at 0 °C over a range of initial anisole concentrations from 0.09 to 0.64 M and over a range of initial SO_4F^- concentrations from 0.009 to 0.055 M. [d] With AMAR Reagent Grade toluene. [e] With Phillips Research Grade toluene. BDH "Aristar" toluene gave the same rate law but a lower and somewhat inconsistent constant. [f] Unsatisfactory kinetic plots at the lower substrate concentration. [g] Reaction was autocatalytic. Rate law and constants are based on initial rates. The functional form of the rate law cannot be considered well established.

(7), 83 (100), 58 (20), 55 (94), 53 (12), 43 (87). This species represented 52% of the methylated product. The other major GC peak (48% of methylated product) could not be identified from its mass spectrum.

Fluorobenzene. ^{19}F NMR of the crude reaction *o*- showed the formation of *o*- and *p*-difluorobenzene, along with an unidentified signal at 150.1 ppm. No *m*-difluorobenzene was detected. High-pressure LC (CH_3OH/H_2O, 50/50 v/v) showed 12% consumption of fluorobenzene (corrected for the overlapping *p*-difluorobenzene peak on the basis of ^{19}F NMR data) and also showed a number of unidentified polar products.

Methyl Benzoate, Benzonitrile, and Nitrobenzene. These compounds react very slowly with fluoroxysulfate. Therefore a high concentration of substrate (1.0 M) was employed, and $RbSO_4F$ was used instead of the cesium salt to permit an increase in reagent concentration to 0.1 M. After reaction was complete, the reaction mixtures were concentrated and analyzed by ^{19}F NMR. Low yields of fluorinated products were detected.

Naphthalene. Fluoroxysulfate in acetonitrile reacts very readily with naphthalene to form both fluorinated and oxygenated products. High-pressure LC ($MeOH/H_2O$, 70/30 v/v) showed 65% consumption of naphthalene and indicated the formation of α-fluoronaphthalene, along with a complex cluster of polar components. An α-fluoronaphthalene fraction was actually isolated from the crude product by column chromatography on silica gel, using petroleum ether as eluant, and its identity was confirmed by ^{19}F NMR. ^{19}F NMR also showed the presence of β-fluoronaphthalene in the reaction mixture.

Solid-probe and high-resolution mass spectrometric analysis indicated that the polar reaction products consisted of a mixture of naphthols, fluoronaphthols, naphthoquinones, fluoronaphthoquinones, and products resulting from addition of F and OH. The crude reaction mixture in acetonitrile was extracted with hexane, which removed naphthalene and fluoronaphthalene, and the polar materials left in the acetonitrile layer were subjected to methylation with dimethyl sulfate/potassium carbonate in anhydrous acetone.[14] GCMS after methylation did not detect any ring degradation product.

Gas Evolution Experiments. Experiments in which the evolution of gases was to be measured were carried out in glass vessels shaped like inverted Y's. The fluoroxysulfate solution was placed in one leg of the vessel and a solution of the substrate in the other. The vessels were evacuated, and the solutions were outgassed and then mixed. After reaction was complete, any evolved gas was pumped through a Dry Ice trap into a collection bulb, using a Toepler pump. The quantity of gas was determined manometrically and its composition by mass spectrometry.

Determination of Relative Reactivities. Relative reactivities were determined by measurement of the rate of consumption of fluoroxysulfate oxidizing power in solutions containing at least a fourfold excess of substrate and usually more than an eightfold excess. Reactions were generally followed to at least 90% of completion and usually gave satisfactory fits to the empirical rate law. Except where otherwise noted, all reactions were carried out at 25.0 °C. Reactions were not run in the dark, but a few were run in brown bottles without significant change in the results. A nitrogen blanket was used to minimize the effect of atmospheric moisture, but no effort was made to exclude air rigorously. The empirical rate laws and details of reaction conditions are given in Table I.

The use of high-purity toluene changed the empirical rate law for the toluene reaction, as is shown in the Table, although it did not alter the product yields. The reaction of benzene, on the other hand, was unaffected by the use of repurified acetonitrile or of Phillips Research Grade benzene. The rate of the benzene reaction was also unaffected by the presence of 0.02 M 1,3,5-trinitrobenzene. The phenol reaction was unaffected by the use of high purity phenol, nor was the anisole reaction affected by the use of repurified anisole.

Results

Product yields for the reactions of SO_4F^- with aromatic substrates are given in Table II. Only in the case of naphthalene were any addition products observed. The approximate relative reactivities of benzene and a number of monosubstituted benzenes appear in Table III. Because the phenol and toluene reactions obey rate laws different from that obeyed by the benzene reaction, the relative reactivities of these substrates will depend on the conditions under which comparisons are made. The reactivity of toluene is made additionally uncertain by the fact that different batches of toluene give different reaction rates and rate laws, while the ill-defined rate laws for the reactions of benzonitrile and nitrobenzene make the reactivities of these substrates also quite uncertain.

An attempt was made to influence the relative extent of ring and side-chain fluorination of toluene by carrying out the reaction in fully deuterated acetonitrile. Both normal and fully deuterated toluene were used as substrates in CD_3CN, but no significant change in yields was observed.

As we have already noted, solutions of rubidium and cesium fluoroxysulfate in acetonitrile appear to be stable over a working day. Over longer periods, an apparently autocatalytic reaction takes place. A typical solution may show 20–40% decomposition over 24 h and will usually be more or less completely decomposed in 3 days. Analysis of the gases evolved during the decomposition indicates the formation of about 0.12 mol of CO_2 and 0.1 mol of HCN for each mol of SO_4F^- decomposed. The decomposition results in the formation of a precipitate that ^{19}F NMR shows to be mostly the alkali fluorosulfate. However it contains about 10% of the initial oxidizing power of the solution in the form of peroxydisulfate.

The reaction of SO_4F^- with aromatic substrates also forms a precipitate, which appears to consist primarily of a mixture of the alkali bisulfate and fluorosulfate. In several cases however, the precipitate also contains a small amount of organic material. The reactions of benzene and the less reactive substituted benzenes produce peroxydisulfate to the extent of 3–10% of the initial oxidizing power, while only traces of peroxydisulfate ($\leq$1%) are formed in the reactions of naphthalene and the substituted benzenes that are more reactive than benzene itself. There is evidence of trace formation of H_2O_2 ($\leq$1% of initial oxidizing power) as indicated by molybdate-catalyzed reaction with iodide. No significant gas evolution is observed in the reaction of fluoroxysulfate with benzene, fluorobenzene, toluene, or biphenyl.

Discussion

The reactions of fluoroxysulfate with aromatic compounds show a number of unusual features that must be considered in the

Table II. Reaction of SO_4F^- with Aromatic Compounds in Acetonitrile[a]

substrate			product yields (% of $[SO_4F^-]_0$)			
			fluoroaromatics			
compd	initial concn, M	stoichiometry $\Delta[\text{substrate}]/[SO_4F^-]_0$	ortho (or α)	meta (or β)	para	other
phenol	0.07	0.71	55	<0.15	4	quinone (1), difluorophenols (5)
phenol[b]	0.1	0.75	68	*c*	6	difluorophenols (3)
phenol[d]	0.14	⩾0.92[e]	83	<0.3	8	*c*
anisole	0.07	0.67	39	<0.15	12	quinone (4.5)
anisole[b]	0.07	0.66	45	*c*	14	*c*
anisole	0.7	⩾0.65[e]	50	<0.3	15	*c*
toluene	0.07	0.50	6	<0.3	1	benzyl fluoride (40) difluorotoluene (2)
toluene[b]	0.07	⩾0.73[e]	10	<0.3	3	benzyl fluoride (60)
toluene	0.66	⩾0.73[e]	4	<0.2	2	benzyl fluoride (67)
biphenyl	0.08	0.35	10	0.3	5	tetraphenyl
biphenyl[b]	0.08	*c*	10	0.5	4	*c*
biphenyl[f]	0.5	*c*	12	<0.4	4	*c*
benzene	0.08	0.27	monofluorobenzene (12)[g]			ring opening[h]
fluorobenzene	0.07	0.12	2	<0.3	4	polar[h]
fluorobenzene[b]	0.08	0.14	4	<0.3	7	*c*
fluorobenzene	0.74	*c*	8	<0.5	8	*c*
methyl benzoate[i]	1.0	*c*	2.0	2.4	0.7	*c*
methyl benzoate[b,i]	1.0	*c*	2.4	2.8	0.8	*c*
benzonitrile[i]	1.0	*c*	0.4	0.4	0.4	*c*
benzonitrile[b,i]	1.0	*c*	0.9	0.7	0.5	*c*
nitrobenzene[i]	1.0	*c*	0.6	0.9	0.2	*c*
nitrobenzene[b,i]	1.0	*c*	0.7	1.2	0.2	*c*
naphthalene	0.09	0.65	19	0.3		polar[h]

[a] At 20–25 °C. Unless otherwise specified $[SO_4F^-]_0 \simeq 0.075$ M. [b] With 0.02–0.025 M 1,3,5-trinitrobenzene. [c] Not determined. [d] $[SO_4F^-]_0 = 0.025$ M. [e] Sum of observed products. [f] $[SO_4F^-]_0 = 0.05$ M. [g] Yield unaffected by the presence of 0.02 M 1,3,5-trinitrobenzene or when benzene concentration was raised to 0.7 M. [h] See Experimental Section. [i] $[SO_4F^-]_0 \simeq 0.1$ M.

Table III. Relative Reactivities of Benzene and Monosubstituted Benzenes toward SO_4F^- in Acetonitrile

substrate	reactivity[a]	substrate	reactivity[a]
phenol	440[b] 740[c]	benzene	1.00
anisole	190	fluorobenzene	0.55
toluene	13–29[b,d] 41–90[d,e]	methyl benzoate	0.17
biphenyl	11	benzonitrile	0.07
		nitrobenzene	0.02_8

[a] $d[SO_4F^-]/dt$ compared to benzene reaction at 25 °C, calculated on the assumption that all reactions have the same rate law except for those of phenol and toluene. [b] Compared to benzene reaction for $[SO_4F^-]_0 \simeq [\text{substrate}]_0 \simeq 0.07$ M. [c] Compared to benzene reaction for $[SO_4F^-]_0 = 0.025$ M. [d] Different sources of toluene give results corresponding to reactivities that differ by a factor of 2. [e] Compared to benzene for $[SO_4F^-]_0 = 0.07$ M and $[C_7H_8]_0 = 0.66$ M.

development of any comprehensive reaction scheme.

The reactions display complex kinetic behavior and span a substantial range of reactivity. Between nitrobenzene and phenol the gross reactivity increases by a factor of 2000. The reaction stoichiometry also varies, as does the yield of fluorinated products, but these variations are considerably less than the variations in reactivity. As one goes to more activated substrates, the yields of fluorinated products increase and the stoichiometry approaches unity.

Toluene reacts to form benzyl fluoride as the principal product, and the fact that all of the consumed toluene can be accounted for while the stoichiometric ratio is only 0.5 points to induced attack of the reagent on the solvent. Nor can attack on the solvent be ruled out in other reactions. However, the fact that no gases are evolved in these reactions means that the mode of attack on the solvent must be quite different from the reaction that takes place between SO_4F^- and acetonitrile in the absence of aromatic substrate. Solvent involvement has also been observed in the reactions of F_2 with organic compounds in acetonitrile.[3]

The ortho isomer tends to predominate in the reactions of the more reactive aromatics, and the yields of the meta isomer are extremely small. *p*-Difluorobenzene is the principal fluorinated product from fluorobenzene, while nitrobenzene and methyl benzoate are predominantly meta directing. Benzonitrile, on the other hand, produces comparable amounts of the three fluoroproducts. Introduction of trinitrobenzene increases the yields of the fluorinated products in most of the reactions, but it does not grossly affect their distribution, and raising the substrate concentration seems to have a roughly parallel effect. The formation of peroxydisulfate in the reaction mixture points to the presence of SO_4^- radical ions.

We may compare our results with data that are available for aromatic substitution by molecular fluorine.[3,4] A very elegant systematic study of yields and relative reactivities has recently been carried out under conditions such that only an extremely small amount of reaction takes place.[4] The isomer distributions with ortho, para-directing monosubstituted benzenes are not too different from those that we have observed with SO_4F^-, but a somewhat more pronounced enhancement of the yield of the *m*-fluoroproduct is reported for the reactions of F_2 with meta-directing substrates. Benzyl fluoride is formed in significant quantities from the reaction of F_2 with toluene,[4] but it is not the predominant product as it is in the case of the fluoroxysulfate reaction. Fluorine also differs from SO_4F^- in that it produces substantial yields of both α and β-fluoronaphthalene from naphthalene ($\alpha:\beta = 3:1$).[3]

The reactions of xenon difluoride with aromatic compounds have also been studied in considerable detail,[7,16] and several differences are evident between XeF_2 and SO_4F^-. For all but the most activated aromatics, the xenon difluoride reaction must be initiated by HF. Fluorination of activated aromatics by XeF_2 favors formation of the para isomers, except in the case of phenol, in which a high meta yield is obtained. Benzyl fluoride is not a significant product from the fluorination of toluene. On the other hand, biphenyl is a byproduct of the reaction between XeF_2 and benzene, whereas it is not formed in the SO_4F^- reaction (although

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(16) (a) Anand, S. P.; Quaterman, L. A.; Hyman, H. H.; Migliorese, K. G.; Filler, R. *J. Org. Chem.* **1975**, *40*, 807. (b) Anand, S. P.; Quarterman, L. A.; Christian, P. A.; Hyman, H. H.; Filler, R. *J. Org. Chem.* **1975**, *40*, 3796.

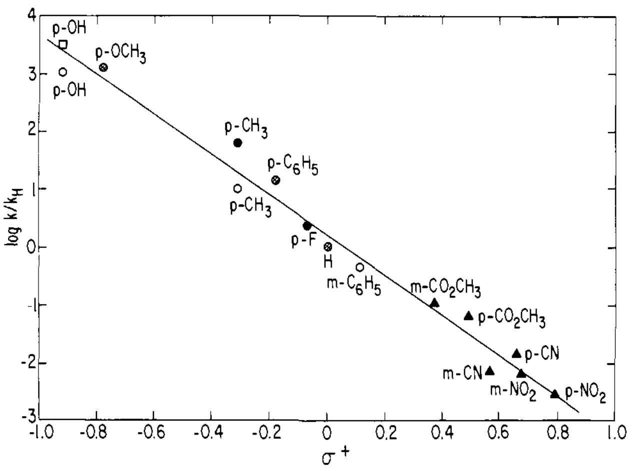


Figure 1. Correlation of σ^+ with relative partial rate factors k/k_H for fluorination by SO_4F^-. Values of k/k_H are derived from data in Tables II and III for conditions under which kinetic and yield data are available or can be readily extrapolated. Values of σ^+ are taken from ref 16. Initial concentrations are as follows: ⊕, average of experiments with $[SO_4F^-]_0 \simeq 0.07$ M, $[\text{substrate}]_0 = 0.07$–$0.7$ M; ○, $[SO_4F]_0 \simeq [\text{substrated}]_0 = 0.07$–$0.08$ M; ●, $[SO_4F^-]_0 \simeq 0.07$ M, $[\text{substrate}]_0 = 0.7$ M; ▲, $[SO_4F^-]_0 = 0.1$ M, $[\text{substrate}]_0 = 1$ M; □, $[SO_4F^-]_0 = 0.025$ M, $[\text{substrate}]_0 = 0.14$ M. In the case of toluene, the ranges of reactivities shown in Table III were averaged for each initial toluene concentration. The straight line is a least-squares fit with slope $\rho^+ = -3.50$ and a correlation coefficient of 0.994.

the latter reagent does form tetraphenyl from biphenyl). Like F_2 but unlike SO_4F^-, XeF_2 reacts with naphthalene to produce significant quantities of both α- and β-fluoronaphthalenes (α:β = 5:1).

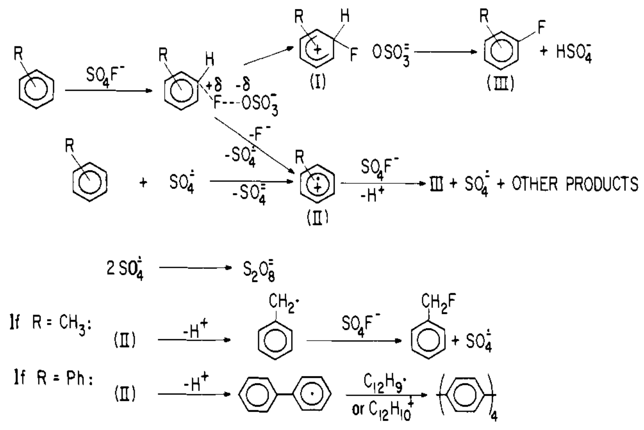
All in all, we conclude that fluorination with SO_4F^- probably involves a mechanism that is at least somewhat different from those involved in fluorinations with XeF_2 or molecular fluorine. The F_2 fluorinations are considered to be electrophilic processes involving arenium ions,[3,4] while for the XeF_2 reactions a mixed mechanism has been proposed in which an initially produced π complex can go on to form either an arenium ion or a radical cation.[17]

What, then, can we say about the mechanism of the fluoroxysulfate reaction? A number of our observations point to the involvement of free radicals: the complex kinetics, the formation of benzyl fluoride and tetraphenyl, the degradation of the benzene ring, the absence of meta-direction in the reaction with benzonitrile, the apparent induced attack on solvent, the enhanced yields in the presence of trinitrobenzene, and the production of $S_2O_8^{2-}$. On the other hand, the vanishingly small yields of meta (or β) fluorinated products obtained from ortho, para-directing substrates, the enhanced meta yields from methyl benzoate and nitrobenzene, and the wide range of reaction rates are more typical of an electrophilic substitution process.

Figure 1 is a Hammett plot of the logarithms of the partial rate factors for production of meta and para fluoroproducts vs. σ^+.[18] The points can be fitted moderately well to a line with slope $\rho^+ = -3.5$. This plot must be regarded as a gross approximation in view of the uncertainties regarding rate laws and the variation of yields with reaction conditions. It does, however, suggest that SO_4F^- is acting as an electrophilic fluorinating agent of relatively low selectivity. Fluoroxysulfate is nevertheless somewhat more selective than molecular F_2, for which a ρ^+ of -2.45 has been reported.[4]

We are inclined to believe that both electrophilic substitution and free-radical processes must be taking place, and we suggest Scheme I as an example of the types of reactions that can at least qualitatively explain our observations. This scheme, which is somewhat similar to the mechanism proposed for XeF_2 fluorination, is meant to imply that the initial steps in these reactions are controlled by the electrophilic character of the reagent, while radical ions can be formed in subsequent steps and can bring about the formation of a variety of products other than the fluorinated aromatic compound. Such free-radical processes tend to predominate with deactivated substrates, for which the arenium cation (I) is relatively unstable, and in the case of toluene, in which the radical cation (II) can readily lose a proton to form a benzyl radical. Ledwith and Russell have observed similar behavior in the reaction of toluene with peroxydisulfate.[19]

Scheme I



The fact that trinitrobenzene increases the yield of fluorinated products from most of the SO_4F^- reactions is consistent with an electrophilic fluorination in competition with free-radical side reactions. It is interesting that trinitrobenzene does not significantly affect the yields of fluorinated products from benzene or biphenyl and that it does not inhibit the production of benzyl fluoride from toluene. It may be that the principal role of the trinitrobenzene is to suppress attack on the solvent. Increasing the substrate concentration may have a similar effect.

Fluoroxysulfate is clearly capable of acting both as an oxidant and as a fluorinating agent. It is therefore noteworthy that fluorination predominates in such an easily oxidized compound as phenol. Oxidation, however, is usually a free-radical process, which we would expect to be considerably less selective than an electrophilic substitution. Hence the net effect of the hydroxyl group on the aromatic ring is to favor electrophilic fluorination at the expense of oxidation.

The extremely high ortho/para ratio that we observe in the products of the phenol reaction is also remarkable. It may reflect direction of the fluorination process by hydrogen bonding between the SO_4F^- and the phenolic proton. In this regard it is worth pointing out that the fluoroxysulfate ion may be unique in that it is an *anionic* electrophile.

Mixed mechanisms of the type shown in Scheme I may have widespread validity for the reactions of powerful fluorinating agents with aromatic compounds, because of the ease with which free radicals can be formed from such reagents. Thus, while it appears that the initial attack of molecular F_2 on aromatics also proceeds by electrophilic substitution, this step can only be isolated at low temperatures and high dilution.[3,4] Free-radical processes are almost certainly responsible for the addition and polymerization reactions that take place under more normal conditions.

Acknowledgment. High-resolution mass spectrometric measurements were made by Mr. Robert Scott, and mass spectrometric gas analyses were carried out by Mrs. A. G. Engelkemeir. A portion of the work on naphthalene was accomplished by Mr. William R. Winchester during his tenure as an undergraduate research participant. We acknowledge a special debt to Mr. Art Kostka for his invaluable assistance in carrying out the NMR measurements, and we wish to thank Dr. Ryoichi Hayatsu, Dr. Kenneth Migliorese, and Dr. Weldon Brown for innumerable helpful discussions.

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