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Kinetics and Mechanism of the Gas-Phase Reaction of Cl Atoms and OH Radicals with Fluorobenzene at 296 K

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Smog chamber/FTIR techniques were used to study the kinetics and mechanism of the reaction of Cl atoms and OH radicals with fluorobenzene, C_6H_5F, in 700 Torr of N_2 or air diluent at 296 K. Reaction of Cl atoms with C_6H_5F proceeds via two pathways: H-atom abstraction to give HCl and the C_6H_4F radical and adduct formation to give the $C_6H_5F{-}Cl$ adduct. At 296 K the rate constant for the abstraction channel is $k_{5a}(Cl + C_6H_5F) = (1.1 \pm 0.1) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. The $C_6H_5F{-}Cl$ adduct undergoes rapid ($k \sim 10^8$ s^{-1}) decomposition to reform C_6H_5F and Cl atoms and reaction with Cl atoms via a mechanism which, at least in part, leads neither to production of C_6H_5Cl nor to reformation of C_6H_5F. As the steady-state Cl atom concentration is increased, the fraction of the $C_6H_5F{-}Cl$ adduct undergoing reaction with Cl atoms increases causing an increase in the effective rate constant for the reaction of C_6H_5F with Cl atoms. The equilibrium between Cl atoms, C_6H_5F, and the $C_6H_5F{-}Cl$ adduct is established rapidly and has an equilibrium constant estimated to be $K_{5b}=[C_6H_5F{-}Cl]/[C_6H_5F][Cl] = (3.2 \pm 2.4) \times 10^{-18}$ cm^3 molecule^{-1}. An upper limit of $k_9 < 6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} was established for the reaction of the $C_6H_5F{-}Cl$ adduct with O_2. The reaction of OH radicals with C_6H_5F was studied and a rate constant of $k(OH + C_6H_5F) = (7.9 \pm 2.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} was determined. The results are discussed with respect to the available literature concerning reaction of Cl atoms and OH radicals with aromatic compounds. As part of this work, rate constants for reaction of OH radicals with 2-, 3-, and 4-fluorophenol of $(6.3 \pm 1.3) \times 10^{-12}$, $(2.3 \pm 0.5) \times 10^{-11}$, and $(2.5 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} were determined.

1. Introduction

Aromatic compounds constitute a significant fraction of the reactive hydrocarbons found in vehicle exhaust and urban air. An understanding of their atmospheric chemistry is needed to assess the environmental impact of vehicle emissions. Unfortunately, significant uncertainties exist in our understanding of the atmospheric oxidation mechanisms and hence environmental impact of aromatic species.[1,2] Atmospheric oxidation of aromatic compounds is initiated by reaction with OH radicals. In smog chamber studies of the atmospheric degradation mechanisms of organic compounds, it is often convenient to use Cl atoms as a surrogate for OH radicals to initiate the sequence of photooxidation reactions. Kinetic and mechanistic data concerning the reaction of Cl atoms with aromatic compounds are needed to design and interpret such smog chamber studies. We have reported such data for C_6H_6,[3] C_6H_5Cl,[3] C_6H_5Br,[4] and C_6H_5I.[5] To complete our investigation of the reactivity of monohalobenzenes, we report here a study of the reaction of Cl atoms with C_6H_5F in 700 Torr of N_2 diluent at 296 K. The kinetics of the reaction of OH radicals with C_6H_5F were also studied as part of this work.

2. Experimental Section

Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[6] The reactor was surrounded by 22 fluorescent blacklamps (GE F40BLB), which were used to generate Cl atoms by photolysis of Cl_2:

$$Cl_2 \xrightarrow{h\nu} 2\,Cl \tag{1}$$

OH radicals were generated by UV irradiation of CH_3ONO/NO/air mixtures:

$$CH_3ONO \xrightarrow{h\nu} CH_3O + NO \tag{2}$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

Reactant and product concentrations were monitored using in situ Fourier transform infrared spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. Calibrated reference spectra were acquired by expanding known

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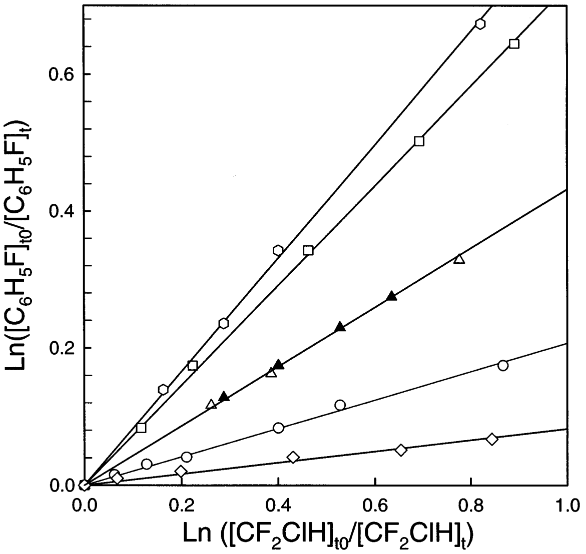


Figure 1. Decay of C_6H_5F versus CF_2ClH in the presence of Cl atoms in 700 Torr of N_2 diluent. The steady-state Cl atom concentrations were (in units of 10^{12} cm^{-3}) 0.52 (diamonds), 2.0 (circles), 3.9 (filled and open triangles), 6.3 (squares), and 8.5 (hexagons).

volumes of reference materials into the chamber. The IR features used for analysis were C_6H_5F (1238, 754, 685 cm^{-1}), CF_2ClH (1312 cm^{-1}), CD_4 (995 cm^{-1}), C_6H_6 (674 cm^{-1}), C_2H_4 (2988, 949 cm^{-1}), C_3H_6 (912 cm^{-1}), 2-chlorofluorobenzene (1030 cm^{-1}), 3-chlorofluorobenzene (892, 862 cm^{-1}), 4-chlorofluorobenzene (830 cm^{-1}), 2-fluorophenol (1174−1266 cm^{-1}), 3-fluorophenol (1129 cm^{-1}), and 4-fluorophenol (1171 cm^{-1}). Experiments were performed at 296 K in 700 Torr of N_2, O_2, or air diluent. All reactants were obtained from commercial sources at purities >99%. Ultrahigh purity nitrogen and air diluent gases were used as received. The samples of fluorobenzene, chlorofluorobenzene, and fluorophenol were subjected to several freeze−pump−thaw cycles before use. In smog chamber experiments, unwanted loss of reactants and products via photolysis and heterogeneous reactions has to be considered. Control experiments were performed in which product mixtures obtained after UV irradiation of $C_6H_5F/Cl_2/N_2$ mixtures were allowed to stand in the dark in the chamber for 15 min. There was no observable (<2%) loss of reactants or products, showing that heterogeneous reactions are not a significant complication in the present experiments. Analysis of the IR spectra was achieved through a process of spectral stripping in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum.

3. Results and Discussion

3.1 Relative Rate Study of $k(Cl + C_6H_5F)$ in 700 Torr of N_2.

The kinetics of reaction 5 were measured relative to reactions 6 and 7:

$$Cl + C_6H_5F \rightarrow \text{products} \tag{5}$$

$$Cl + CF_2ClH \rightarrow \text{products} \tag{6}$$

$$Cl + CD_4 \rightarrow \text{products} \tag{7}$$

Initial reactant concentrations were 3.5−4.5 mTorr of C_6H_5F, 0.15−6.5 Torr of Cl_2, and 4.5−15 mTorr of either CF_2ClH or CD_4 in 700 Torr of N_2 diluent. Typical data showing the observed loss of C_6H_5F versus that of CF_2ClH following UV irradiation of six different $C_6H_5F/CF_2ClH/Cl_2/N_2$ mixtures are shown in Figure 1. The lines through the data in Figure 1 are linear fits which give values of k_5/k_6. As seen from Figure 1, different values of k_5/k_6 are obtained from experiments performed under different experimental conditions. This observation is not consistent with the simple chemistry depicted above in which C_6H_5F is consumed via reaction with Cl atoms and not reformed in any process.

It has been shown[3] that the reactions of Cl atoms with C_6H_6 and C_6H_5Cl do not proceed via a simple mechanism such as that depicted in reaction 5. Reaction of Cl atoms with C_6H_6 and C_6H_5Cl proceeds via two channels, hydrogen atom abstraction and adduct formation. The adduct decomposes rapidly to reform the aromatic compound and reacts with Cl atoms to give products other than the aromatic reactant. In C_6H_5F we can represent this chemistry as

$$Cl + C_6H_5F \rightarrow C_6H_4F + HCl \tag{5a}$$

$$Cl + C_6H_5F \rightarrow C_6H_5F{-}Cl \tag{5b}$$

$$C_6H_5F{-}Cl \rightarrow Cl + C_6H_5F \tag{−5b}$$

$$C_6H_5F{-}Cl + Cl \rightarrow \text{products} \tag{8a}$$

It is possible that some fraction of the reaction of the $C_6H_5F{-}Cl$ adduct with Cl atoms proceeds to regenerate C_6H_5F and Cl_2, constituting a C_6H_5F-catalyzed recombination of Cl atoms:

$$C_6H_5F{-}Cl + Cl \rightarrow C_6H_5F + Cl_2 \tag{8b}$$

The following differential equations describe the temporal behavior of C_6H_5F and $C_6H_5F{-}Cl$:

$$\frac{-\partial[C_6H_5F]}{\partial t} = k_{5a}[Cl][C_6H_5F] + k_{5b}[Cl][C_6H_5F] - k_{-5b}[C_6H_5F{-}Cl] - k_{8b}[Cl][C_6H_5F{-}Cl] \tag{i}$$

$$\frac{\partial[C_6H_5F{-}Cl]}{\partial t} = k_{5b}[Cl][C_6H_5F] - k_{-5b}[C_6H_5F{-}Cl] - k_8[Cl][C_6H_5F{-}Cl] \tag{ii}$$

where $k_8 = (k_{8a} + k_{8b})$.

Application of the steady-state approximation for the $[C_6H_5F{-}Cl]$ adduct gives

$$\frac{-\partial\,[C_6H_5F]}{\partial t} = k_{5a}[Cl]_{SS}[C_6H_5F] + \frac{k_{5b}k_{8a}[Cl]^2{}_{SS}\,[C_6H_5F]}{(k_{-5b} + k_8[Cl]_{SS})} \tag{iii}$$

In the experiments performed in this work, we measure an effective rate constant for reaction 5 given by

$$\frac{-\partial[C_6H_5F]}{\partial t} = k_{\text{effective}}[Cl]_{SS}[C_6H_5F] \tag{iv}$$

Hence

$$k_{\text{effective}} = k_{5a} + \frac{k_{5b}k_{8a}[Cl]_{SS}}{(k_{-5b} + k_8[Cl]_{SS})} \tag{v}$$

We can now consider the two extremes of behavior depending on the relative magnitude of k_{-5b} and $k_8[Cl]_{ss}$. If $k_8[Cl]_{ss} \gg k_{-5b}$, then expression v can be reduced to $k_{\text{effective}} = k_{5a} + k_{5b}k_{8a}/k_8$ and no dependence on Cl atom steady-state concentration would be observed. If $k_8[Cl]_{ss} \ll k_{-5b}$, then the effective rate constant

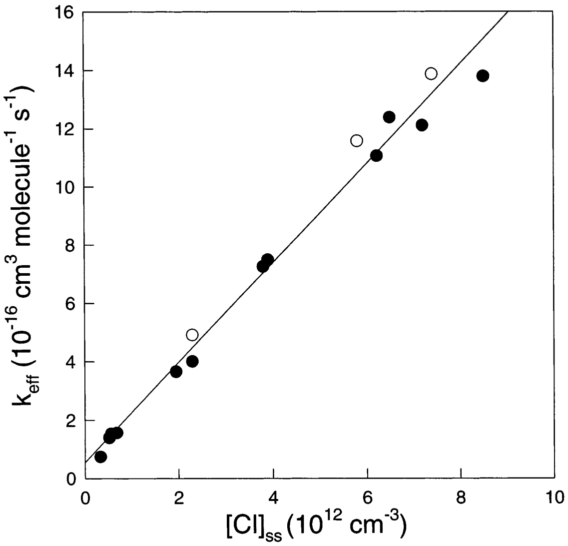


Figure 2. Effective rate constants, k_{eff}, for the reaction of Cl atoms with C_6H_5F measured using CF_2ClH (filled symbols) and CD_4 (open symbols) references in 700 Torr N_2 diluent versus the steady-state Cl atom concentration.

would be linearly dependent on $[Cl]_{ss}$ and $k_{effective}$ given by the expression:

$$k_{effective} = k_{5a} + \frac{k_{5b}k_{8a}[Cl]_{SS}}{k_{-5b}} \qquad (vi)$$

The Cl atom steady-state concentration, $[Cl]_{ss,}$ was varied in the present work by changing the initial concentration of molecular chlorine and the intensity of UV irradiation. The chlorine atom concentration was calculated from the observed decay of the reference compounds (CF_2ClH or CD_4) using expression vii:

$$[Cl]_{SS} = \left(\frac{1}{t \times k_{reference}}\right) \mathrm{Ln}\left(\frac{[reference]_{t0}}{[reference]_t}\right) \qquad (vii)$$

where t is the time of irradiation in seconds, $k_{reference}$ is the reference rate constant (k_6 or k_7), and $[reference]_{t0}$ and $[reference]_t$ are the concentrations of the reference compounds before and after the irradiation. Use of expression vii to calculate $[Cl]_{ss}$ relies on the following assumptions: (1) reference compounds are solely lost via reaction with Cl atoms, (2) literature values for k_6 and k_7 are accurate, (3) UV blacklights provide uniform illumination of the reaction mixtures, and (4) Cl atoms have a lifetime which is short compared to the UV irradiation time. These assumptions are discussed and validated elsewhere.[3]

For a given $[Cl]_{ss}$ variation of the initial molecular chlorine concentration, UV irradiation intensity and initial reactant concentrations had no systematic effect on the rate constant ratios obtained. For example, the data shown in Figure 1 by filled triangles were obtained in an experiment employing an initial Cl_2 concentration 4 times higher and a UV irradiation intensity 4 times lower than that used to measured the data indicated by the open triangles. The steady-state Cl atom concentrations, $[Cl]_{ss}$, in the two experiments were indistinguishable within the experimental uncertainties. Even though the initial molecular chlorine concentrations and light intensity were very different, the results from both experiments fall on the same line.

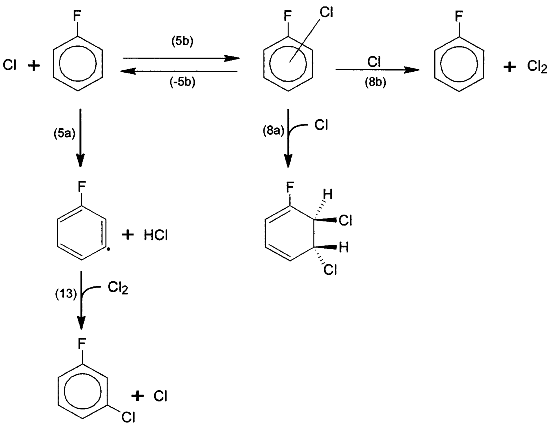


Figure 3. Reaction scheme describing the chemistry occurring following reaction of Cl atoms with C_6H_5F. For simplicity only one isomer is shown in reactions 5a and 8a.

Figure 2 shows a plot of $k_{effective}$ (k_5/k_6 and k_5/k_7 measured herein multiplied by $k_6 = 1.7 \times 10^{-15}$ [3] and $k_7 = 6.1 \times 10^{-15}$ [7] cm^3 molecule^{-1} s^{-1}) versus $[Cl]_{ss}$. Inspection of Figure 2 reveals that for a given $[Cl]_{ss}$ there is no discernible difference between values of $k_{effective}$ derived from experiments employing either CHF_2Cl or CD_4 as reference compounds. As seen from Figure 2, the "effective reactivity" of Cl atoms toward C_6H_5F increases linearly with the steady-state Cl atom concentration.

The simplest and most plausible explanation for the behavior observed in Figure 2 is that the reaction of Cl atoms with C_6H_5F follows the same mechanism as that of the reaction of Cl atoms with benzene and chlorobenzene.[3] Hence, we postulate that the reaction of Cl atoms with C_6H_5F proceeds via two channels: H-atom abstraction (5a) to give HCl and the C_6H_4F radical and addition (5b) to give a C_6H_5F-Cl adduct. The adduct can undergo decomposition to reform reactants (−5b) or react further with Cl atoms in a manner which does not regenerate C_6H_5F (8a). The reaction scheme is shown in Figure 3. The linearity of the plot of $k_{effective}$ versus $[Cl]_{ss}$ in Figure 2 indicates that decomposition via reaction (−5b) is the dominant fate of the $[C_6H_5F-Cl]$ adduct.

Linear least-squares analysis of the data in Figure 2 gives an intercept of $k_{5a} = (5.1 \pm 5.4) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} and a slope of $(k_{5b}k_{8a})/k_{-5b} = (1.71 \pm 0.14) \times 10^{-28}$cm^3 molecule^{-1} s^{-1}, quoted uncertainties are two standard deviations from the linear regressions. The value of k_{5a} derived in this analysis is indistinguishable from zero and hence we derive an upper limit of $k_{5a} < 1.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} The value of $(k_{5b}k_{8a})/k_{-5b}$ can be used to estimate the equilibrium constant $K_{5b} = k_{5b}/k_{-5b}$. Reactions of alkyl radicals (e.g., CH_3,[8] C_2H_5,[8] and C_6H_5[9]) with Cl atoms proceed with rate constants which are close to the gas kinetic limit, that is, $(1-5) \times 10^{-10}$ cm^3 molecule^{-1} and it seems reasonable to assume that k_{8a} is likely of similar magnitude. With this assumption, we arrive at an estimate of $K_{5b} = k_{5b}/k_{-5b} = (1.1 \pm 0.8) \times 10^{-18}$ cm^3 molecule^{-1}. The equilibrium between Cl atoms, C_6H_5F, and the adduct C_6H_5F-Cl lies toward Cl atoms and C_6H_5F. It takes a pressure of approximately 30 Torr of C_6H_5F to trap 50% of the Cl atoms in the form of the C_6H_5F-Cl adduct. Clearly, the Cl atom is only weakly bound in the C_6H_5F-Cl adduct. In contrast to the behavior in the gas phase, it is well established that Cl atoms form stable adducts with aromatic compounds in the solution phase. In solution phase studies, it has been observed that Cl atoms add to the aromatic ring with rate constants which are close to the diffusion limit.[10−17] Such observations suggest that reaction 5b proceeds with a rate constant of the order of 10^{-10} cm^3 molecule^{-1} s^{-1} in the gas phase. Proceeding on this assumption leads to an estimate of $k_{-5b} = 9 \times 10^7$ s^{-1}. The

$C_6H_5F{-}Cl$ adduct has a short (approximately 10^{-8} s) lifetime in the gas phase.

3.2 Relative Rate Study of $k(Cl + C_6H_5F)$ in 700 Torr of O_2. To provide insight into the reactions occurring during the Cl atom initiated oxidation of C_6H_5F in air and the effect of O_2 on the kinetics of reaction 5, relative rate experiments were performed to measure k_5/k_6 in 700 Torr of O_2 diluent at 296 K. The reaction mixture used consisted of 10 mTorr of C_6H_5F, 4 mTorr CF_2ClH, and 2.1 Torr Cl_2 in 700 Torr of O_2 diluent. UV irradiation of this gas mixture led to the loss of C_6H_5F and CF_2ClH shown in Figure 4. The solid curve in Figure 4 is a second-order regression to aid visual inspection of the data trend. Unlike the data obtained in N_2 diluent, the relative rate plot obtained in O_2 diluent shows significant curvature. The curvature in Figure 4 indicates that either reactions 5 and 6 are not the sole loss mechanisms for C_6H_5F and CF_2ClH or that there are unknown processes that regenerate C_6H_5F or CF_2ClH. In the presence of 700 Torr of O_2, it is difficult to imagine reactions that regenerate C_6H_5F or CF_2ClH. By comparison with similar systems,[3,18] we believe that the most likely explanation for the observed curvature lies in the generation of OH radicals during the Cl atom initiated oxidation of C_6H_5F. OH radicals react approximately 130 times faster with C_6H_5F than with CF_2ClH[19,20] and their generation will lead to an enhanced rate of C_6H_5F loss. As reaction products build up there will be a competition for the available OH radicals resulting in decreased C_6H_5F loss and curvature of the relative rate plot.

The dotted line in Figure 4 is a linear fit to the first three data points which gives a slope of 0.51 from which an effective value of $k_5 = 8.7 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} can be derived. From the rate of CF_2ClH loss for the experiments shown in Figure 4, the $[Cl]_{ss}$ was calculated to be 1.2×10^{12} cm^{-3}. Figure 2 indicates that with $[Cl]_{ss} = 1.2 \times 10^{12}$ cm^{-3} a value of $k_5 = 2.6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} is expected from the "pure" Cl atom reactions. The initial rate of C_6H_5F loss observed in experiments conducted in 700 Torr of O_2 is 3.3 times that expected on the basis of the results obtained in N_2 diluent. The slope of the relative rate plot in Figure 4 at high consumptions of CF_2ClH and C_6H_5F tends toward the value of k_5/k_6 expected from the "pure" Cl atom reactions. This behavior can be rationalized in terms of increasing loss of OH radicals via reaction with C_6H_5F oxidation products.

The data in Figure 4 contain information concerning the reaction of O_2 with the $C_6H_5F{-}Cl$ adduct. Let us consider two possible reaction pathways:

$$C_6H_5F{-}Cl + O_2 \rightarrow C_6H_4FCl + HO_2 \tag{9a}$$

$$C_6H_5F{-}Cl + O_2 \rightarrow \text{products other than } C_6H_4FCl + HO_2 \tag{9b}$$

Calibrated reference spectra for 2-, 3-, and 4-chlorofluorobenzene were used to search for product features attributable to C_6H_4FCl formed in reaction 9a. No such features were found and we derive an upper limit of 2% for the yield of each of the three isomers. The effect of reaction 9b would be to augment the loss of C_6H_5F, and this reaction may contribute to the "enhanced" loss of C_6H_5F observed in O_2 diluent. There are two points to bear in mind when discussing the potential importance of reaction 9. First, the O_2 concentration is constant and any enhanced rate of C_6H_5F loss would be constant during the experiment. The experimental results shown in Figure 4 show a decrease in the rate of C_6H_5F loss for longer irradiations; thus, reaction of the $C_6H_5F{-}Cl$ adduct with O_2 cannot solely explain the experimental observations. Second, in absolute terms, any "enhancement" caused by reaction of the $C_6H_5F{-}Cl$ adduct with O_2 is modest. An upper limit for $k_9(k_{9a} + k_{9b})$ can be derived by applying the following logic. As discussed above, the initial rate of C_6H_5F loss in 700 Torr air is 3.3 times that expected for the "pure" Cl atom reactions. In the experiments described above in 700 Torr of O_2, the concentration of O_2 was $2.3 \times 10^{19}/1.2 \times 10^{12} = 1.9 \times 10^7$ times greater than that of Cl atoms. Ascribing the entire enhanced fluorobenzene loss to reaction of the adduct with O_2, it follows that a factor of 1.9×10^7 excess of O_2 over Cl atoms increases the benzene loss by an additional 230%. Reaction 8a cannot proceed faster than the gas kinetic limit, $k_{8a} < 5 \times 10^{-10}$, hence $k_9 < 6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. Clearly, reaction of the $C_6H_5F{-}Cl$ adduct with O_2 occurs slowly (if at all).

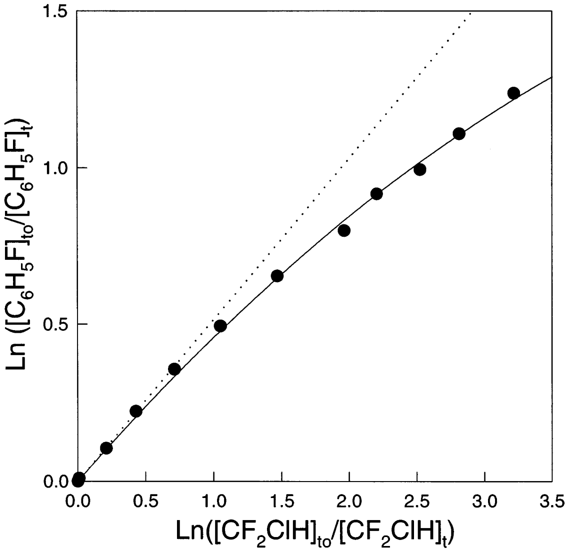


Figure 4. Loss of C_6H_5F versus that of CF_2ClH following exposure to Cl atoms in 700 Torr of O_2.

The reactions occurring during the Cl initiated oxidation of C_6H_5F in O_2 are complex and poorly characterized. The aim of the present work was to elucidate the kinetics of the reaction of Cl atoms with C_6H_5F and not the detailed chemistry associated with the subsequent reactions in air diluent. Experiments in O_2 diluent were not pursued further.

3.3 Relative Rate Study of the OH + C_6H_5F Reaction in 700 Torr of Air. The kinetics of reaction 10 were measured relative to reactions 11 and 12:

$$C_6H_5F + OH \rightarrow \text{products} \tag{10}$$

$$C_6H_6 + OH \rightarrow \text{products} \tag{11}$$

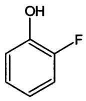
$$C_2H_4 + OH \rightarrow \text{products} \tag{12}$$

Reaction mixtures consisted of 5−14 mTorr of C_6H_5F, 43−106 mTorr CH_3ONO, 1−13 mTorr of reference compound (C_6H_6 or C_2H_4), and 10−13 mTorr NO in 700 Torr of air diluent. The observed loss of C_6H_5F versus those of the reference compounds in the presence of OH radicals is shown in Figure 5. Least-squares analysis of the data in Figure 5 gives $k_{10}/k_{11} = 0.69 \pm 0.05$ and $k_{10}/k_{12} = 0.086 \pm 0.006$, quoted uncertainties are two standard deviations from the linear regressions. Using $k_{11} = (1.22 \pm 0.24) \times 10^{-12}$ [1] and $k_{12} = (8.52 \pm 1.28) \times 10^{-12}$ [21] cm^3 molecule^{-1} s^{-1} gives $k_{10} = (8.4 \pm 1.7) \times 10^{-13}$ and $(7.3 \pm 1.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. We choose to quote a final value for k_{10} which is the average of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_{10} = (7.9 \pm 2.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

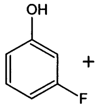
There have been two previous determinations of k_{10}. Ohta and Ohyama[22] used relative rate methods techniques to study reaction 10 in atmospheric pressure of air at ambient temperature. Ohta and Ohyama[22] reported a rate constant ratio of $k(\mathrm{OH} + \mathrm{C_6H_5F})/k(\mathrm{OH} + n\text{-hexane}) = 0.16 \pm 0.02$ and used a value of $k(\mathrm{OH} + n\text{-hexane}) = 5.9 \times 10^{-12}$ to derive the bimolecular rate constant $k(\mathrm{OH} + \mathrm{C_6H_5F}) = (8.7 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Unfortunately, there is an internal inconsistency in the data reported by Ohta and Ohyama.[22] The reference rate constant used by Ohta and Ohyama[22] is correct. However, the rate constant ratio and bimolecular rate constant, k_{10}, are not consistent (the product of 0.16 and 5.9×10^{-12} is 9.4×10^{-12} not 8.7×10^{-12}). It is unclear whether the error lies in the rate constant ratio or bimolecular rate constant, k_{10}. We will not consider the work of Ohta and Ohyama[22] further.

Wallington et al.[19] used flash photolysis resonance fluorescence techniques to determine $k_{10} = (6.31 \pm 0.81) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} in 25−50 Torr of argon diluent at 296 K. The present determination of $k_{10} = (7.9 \pm 2.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} is consistent with the previous findings of Wallington et al.[19] The consistency of the values of k_{10} measured in 700 Torr of air and 25−50 Torr of argon diluent indicates that the kinetics of reaction 10 are insensitive to total pressure and the nature of the diluent gas over the range studied.

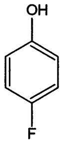
3.4 Relative Rate Study of *k*(OH + Fluorophenol) in 700 Torr of Air. Prior to investigating the products of the reaction of C_6H_5F with OH radicals (see section 3.5), relative rate techniques were used to investigate the reactivity of OH radicals toward fluorophenol. The kinetics of reactions 13, 14, and 15 were measured relative to reactions 12 and 16:



+ OH → products **(13)**



+ OH → products **(14)**



+ OH → products **(15)**

$$\mathrm{C_2H_4} + \mathrm{OH} \rightarrow \text{products} \qquad (12)$$

$$\mathrm{C_3H_6} + \mathrm{OH} \rightarrow \text{products} \qquad (16)$$

Control experiments were performed to check for complications caused by photolysis or heterogeneous loss; no evidence for such complications was observed.

The experimental conditions used in the study of reactions 13−15 were 2.0−3.6 mTorr of fluorophenol, 14−33 mTorr CH_3ONO, 2.8−15 mTorr of reference compound (C_3H_6 or C_2H_4), and 0−15 mTorr NO in 700 Torr of air diluent. The observed loss of fluorophenol versus those of the reference compounds in the presence of OH radicals is shown in Figure 6. Rate constant ratios obtained by linear least-squares analysis of the data in Figure 6 are given in Table 1. Quoted uncertainties are two standard deviations from the linear regressions. Using

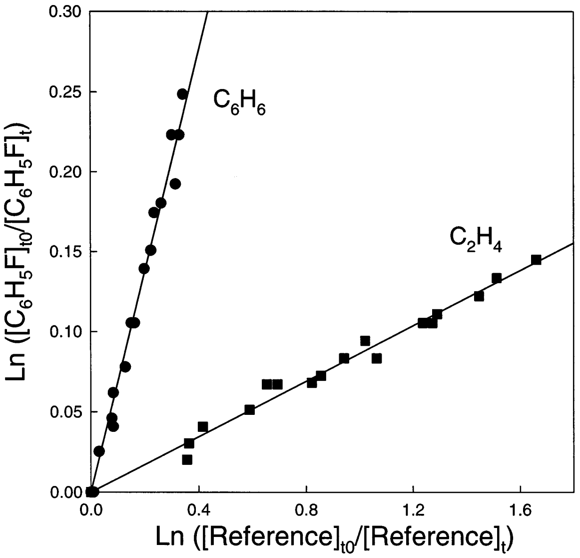


Figure 5. Decay of C_6H_5F versus the reference compounds C_6H_6 (circles) and C_2H_4 (squares) in the presence of OH radicals in 700 Torr of air.

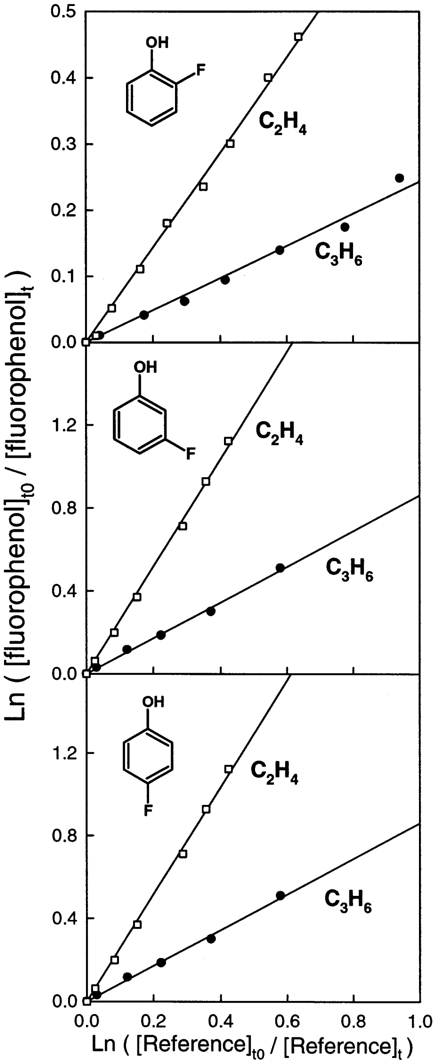


Figure 6. Decay of 2-fluorophenol, 3-fluorophenol, and 4-fluorophenol versus the reference compounds C_2H_4 (open squares) and C_3H_6 (solid circles) in the presence of OH radicals in 700 Torr of air.

$k_{12} = (8.52 \pm 1.28) \times 10^{-12}$ and $k_{16} = (2.63 \pm 0.39) \times 10^{-11}$[21] gives $k_{13} = (6.1 \pm 1.0) \times 10^{-12}$ and $(6.4 \pm 1.2) \times 10^{-12}$, k_{14}

TABLE 1: Rate Constant Ratios, *k*(OH + Fluorophenol)/*k*(OH + Reference), Measured in 700 Torr of Air Diluent

	reference	
aromatic	C_2H_4	C_3H_6
2-fluorophenol	0.718 ± 0.053	0.243 ± 0.026
3-fluorophenol	2.59 ± 0.19	0.861 ± 0.014
4-fluorophenol	2.87 ± 0.25	0.912 ± 0.082

$= (2.2 \pm 0.4) \times 10^{-11}$ and $(2.3 \pm 0.4) \times 10^{-11}$, and $k_{15} = (2.5 \pm 0.4) \times 10^{-11}$ and $(2.4 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. We choose to quote values for k_{13}, k_{14}, and k_{15} which are the averages of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_{13} = (6.3 \pm 1.3) \times 10^{-12}$, $k_{14} = (2.3 \pm 0.5) \times 10^{-11}$, and $k_{15} = (2.5 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. There have been no previous determinations of k_{13}–k_{15}.

The rate constants for the reactions between OH radicals and 3-fluorophenol and 4-fluorophenol, respectively, are 30 times faster than that of the reaction of C_6H_5F with OH radicals and close to the rate constant for the reaction of OH radicals with phenol (2.7×10^{-11} cm^3 molecule^{-1} s^{-11}). It is interesting that the reactivity of 2-fluorophenol toward OH radicals is approximately 4 times lower than those of 3-fluorophenol and 4-fluorophenol. While there is significant intramolecular hydrogen bonding between the −OH and −F substituents in 2-fluorophenol,[23] the molecular geometry in 3- and 4-fluorophenol precludes such interaction. It seems likely that the additional stability conferred by intramolecular hydrogen bonding in 2-fluorophenol lowers its reactivity toward OH radicals. Similar behavior has been reported for the reaction of Cl atoms with chlorophenol isomers.[24]

The reactivity of OH radicals toward fluorobenzene and fluorophenol measured here can be compared to the reactivity predicted from the structure activity relationship (SAR) developed by Kwok and Atkinson[25] and Zetzsch.[26] Reaction of OH radicals with fluorobenzene and fluorophenol is expected to proceed essentially exclusively via addition to the aromatic ring. The rate of the addition channel is related to the sum of the electrophilic substituent constants ($\Sigma\sigma^+$) by the expression:[25]

$$\log k_{\text{add}}\ (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) = -11.71 - 1.34\Sigma\sigma^+$$

Using literature values of $\sigma^{+\,27}$ gives $k_{\text{add}} = 2.44 \times 10^{-12}$, 1.12×10^{-11}, 4.17×10^{-11}, and 1.12×10^{-11} cm^3 molecule^{-1} s^{-1} for fluorobenzene, 2-fluorophenol, 3-fluorophenol, and 4-fluorophenol, respectively (in the absence of an available σ^+ (meta) value for the −OH substituent we assume ortho/para addition). These results differ from the measured values by factors of 3.1, 1.8, 1.8, and 0.4, respectively. Differences of this magnitude are not uncommon when SAR techniques are used to predict kinetic data.

3.5 Product Studies of the Reactions of Cl Atoms and OH Radicals with C_6H_5F. To provide insight into mechanism of the reaction of Cl atoms and OH radicals with C_6H_5F, experiments were performed to determine the products formed following UV irradiation of $C_6H_5F/CF_2ClH/Cl_2/N_2$ and $C_6H_5F/CH_3ONO/NO$/air mixtures, respectively.

Figure 7 shows typical spectra observed before (A) and after (B) a 70-min irradiation of a mixture containing 138 mTorr C_6H_5F, 2.7 mTorr CF_2ClH, and 148 mTorr Cl_2 in 700 Torr N_2 diluent. Panel C shows the product spectrum obtained by subtracting IR features attributable to C_6H_5F and CF_2ClH from panel B. Comparison of the features in panel C with reference spectra of 3- and 4-chlorofluorobenzene given in panels D and E shows that these products are formed. Figure 8 shows a plot of the observed formation of 3- and 4-chlorofluorobenzene versus the loss of C_6H_5F following successive UV irradiations of the $C_6H_5F/CF_2ClH/Cl_2/N_2$ described above. Linear least-squares analysis gives molar yields for 3- and 4-chlorofluorobenzene of 11 ± 1% and 4.1 ± 0.3%, respectively. There was

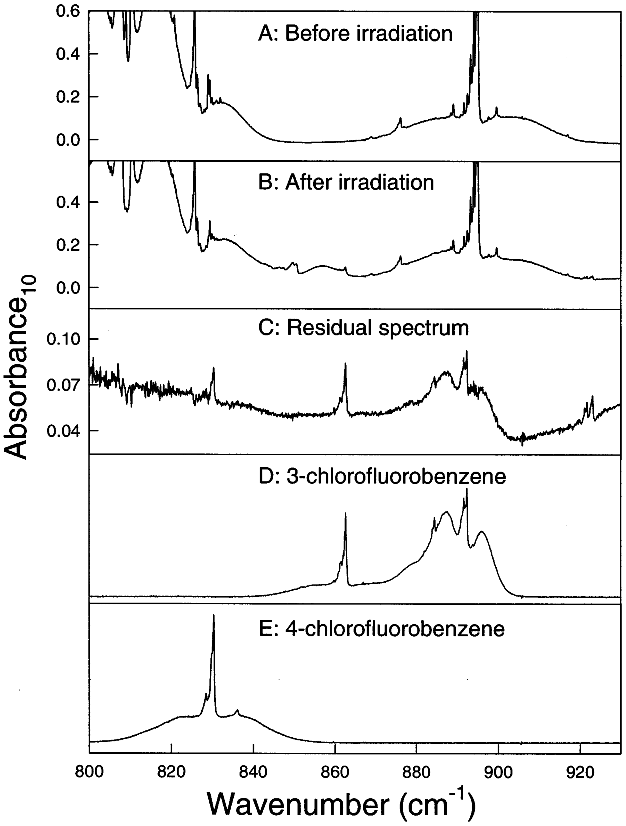


Figure 7. IR spectra acquired before (A) and after (B) a 70-min irradiation of a mixture containing 138 mTorr C_6H_5F, 2.7 mTorr CF_2ClH, and 148 mTorr Cl_2 in 700 Torr of N_2 diluent. Subtraction of features attributable to C_6H_5F and CF_2ClH gives the product spectrum shown in panel C. Reference spectra of 3- and 4-chlorofluorobenzene are shown in panels D and E.

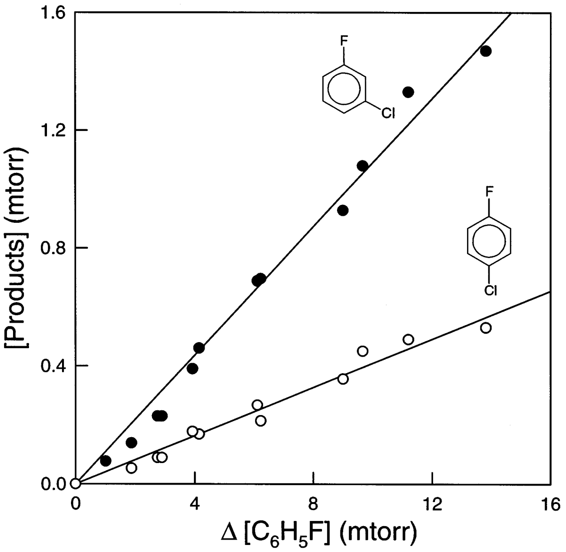


Figure 8. Formation of 3- and 4-chloro fluorobenzene versus loss of C_6H_5F following successive UV irradiations of a reaction mixture containing 138 mTorr C_6H_5F, 2.7 mTorr CF_2ClH, and 148 mTorr Cl_2 in 700 Torr of N_2 diluent.

TABLE 2: Values of k_{5a} and $(k_{5b}k_{8a})/k_{-5b}$ for Gas-Phase Reactions of Cl Atoms with Aromatic Compounds

aromatic	k_{5a}[a]	$(k_{5b}k_{8a})/k_{-5b}$[b]	$K_{5b} = (k_{5b})/k_{-5b}$[c]	k_{-5b}[d]	reference
C_6H_6	1.3 ± 1.0	4.5 ± 1.1	3.2 ± 2.4	3×10^7	3
C_6H_5F	0.11 ± 0.01	1.71 ± 0.14	1.1 ± 0.8	9×10^7	this work
C_6H_5Cl	<2.5	5.3 ± 0.6	3.4 ± 2.5	3×10^7	3

[a] Units of 10^{-16} cm^3 molecule^{-1} s^{-1}. [b] Units of 10^{-28} cm^6 molecule^{-2} s^{-1}. [c] Units of 10^{-18} cm^3 molecule^{-1}, estimated assuming $k_{8a} = (1-5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. [d] Units of s^{-1}, estimated assuming $k_{5b} = 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

no observable formation of 2-chlorofluorobenzene. The detection limit for the 2-chloro isomer (determined by intensity and position of IR features) was greater than that for either the 3- or 4-chloro isomers; we derive an upper limit of 5% for the molar yield of the 2-chloro isomer. From the observed loss of CF_2ClH, it was calculated that for this experiment $[Cl]_{ss} = 3.4 \times 10^{11}$ cm^{-3} (the lowest used in this study), and from the observed loss of C_6H_5F, a rate constant ratio of $k_5/k_6 = 0.043 \pm 0.003$ was derived giving $k_{eff} = (7.3 \pm 0.5) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. Chlorofluorobenzene is formed via the reaction of fluorophenyl radicals, C_6H_4F, with Cl_2 and provides a measure of the fraction of reaction 5 that proceeds via channel 5a:

$$Cl + C_6H_5F \rightarrow C_6H_4F + HCl \tag{5a}$$

$$C_6H_4F + Cl_2 \rightarrow C_6H_4FCl + Cl \tag{17}$$

The sum of the yields of 3- and 4-chlorofluorobenzene, $15.1 \pm 1.3\%$, combined with the value of $k_{eff} = (7.3 \pm 0.5) \times 10^{-17}$ gives $k_{5a} = (1.1 \pm 0.1) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. This result is consistent with the upper limit of $k_{5a} < 1.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} derived in section 3.1.

The values of k_{5a} and $(k_{5b}k_{8a})/k_{-5b}$ measured herein are compared to previous measurements of such parameters for the reaction for Cl atoms with C_6H_6 and C_6H_5Cl in Table 2. It can be seen from Table 2 that Cl atoms abstract hydrogen from C_6H_6, C_6H_5Cl, and C_6H_5F with a rate constant of the order of $10^{-17}-10^{-16}$ cm^3 molecule^{-1} s^{-1}. Hydrogen abstraction from benzene by Cl atoms is endothermic by 32 kJ mol^{-1}.[28] While there are no available data concerning the thermochemistry of reaction 5a, it seems likely that the thermochemistry of this reaction is similar to that of the corresponding reaction with benzene. It has been shown previously that reaction 18 proceeds with an activation barrier close to the reaction endothermicity.[3]

$$Cl + C_6H_6 \rightarrow C_6H_5 + HCl \tag{18}$$

We can use the value of k_{5a} measured herein and an activation energy of 32 kJ mol^{-1} for reaction 5a to arrive at a preexponential A factor of 7×10^{-12} cm^3 molecule^{-1} s^{-1} for reaction 5a. This result is reasonable for hydrogen abstraction from organic compounds by Cl atoms which typically have A factors of $0.5-10 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[8]

From Table 2 it can be seen that the equilibrium constant for reactions 5b and −5b is smaller than those for the corresponding adduct formation in the reactions with C_6H_6 and C_6H_5Cl. Such behavior presumably reflects the strong electron-withdrawing effect of the fluorine substituent which destabilizes the adduct.

It is of interest that the yields of the 2-, 3-, and 4-chlorofluorobenzene isomers are in the approximate ratio <1:2:1. If hydrogen abstraction from each possible site in C_6H_5F occurred statistically then the o/m/p isomer ratio would be expected to be 2:2:1. The relative abundance of the 3- and 4-chloro isomers reflects that expected from purely statistical considerations while the 2-chloro isomer is less abundant than expected. The lower yield of the 2-chloro isomer may reflect the inductive effect of the fluorine atom destabilizing radical centers close to it. In addition to chlorofluorobenzene IR product features of unknown product(s) were observed at 1025, 1800, and 1866 cm^{-1}.

To investigate the products of the OH radical, initiated oxidation of C_6H_5F in 700 Torr of air experiments were conducted using mixtures of 100−343 mTorr of C_6H_5F, 77−155 mTorr of CH_3ONO, and 15 mTorr of NO and with 3.0 mTorr of propene added as a OH radical tracer compound. Consumption of propene was measured and used to calculate the consumption of C_6H_5F. In all experiments, C_6H_5F consumption was limited to <3%. Using reference spectra of 2-, 3-, and 4-fluorophenol and appropriate corrections for secondary reactions with OH radicals (see section 3.4), we were able to determine a yield of $10 \pm 3\%$ for the 4-fluorophenol and upper limits of 3% for both 2-fluoro and 3-fluorophenol. 4-Fluorophenol was the only observed product following the reaction of OH radicals with fluorobenzene.

4. Discussion

4.1 Reaction of Cl Atoms with C_6H_5F. The present work completes our study of the kinetics and mechanisms of the gas-phase reaction of Cl atoms with benzene and the series of monohalobenzenes. As discussed in section 3.2, the kinetics and mechanism (see Figure 3) of the reaction of Cl atoms with C_6H_5F are very similar to those for reaction of Cl atoms with C_6H_6 and C_6H_5Cl (see Table 2). Such reactions proceed slowly with effective rate constants of the order of 10^{-16} cm^3 molecule^{-1} s^{-1} via two reaction channels: hydrogen abstraction and adduct formation with the adduct undergoing rapid decomposition to reform the reactants. In dramatic contrast, the reactions of Cl atoms with C_6H_5Br and C_6H_5I proceed rapidly ($k_{Cl+C6H5Br} = (1.3 \pm 0.2) \times 10^{-11}$, $k_{Cl+C6H5I} = (3.3 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) to give C_6H_5Cl in a yield indistinguishable from 100%.[4,5] At first sight, it appears that the reactions of Cl atoms with C_6H_5Br and C_6H_5I proceed via a different mechanism from those with C_6H_5F and C_6H_5Cl. However, consideration of the thermochemistry associated with these reactions suggests that this might not be the case. The displacement reactions have different thermochemistry. Displacement of the fluorine atom in fluorobenzene is endothermic, will not occur to any significant degree spontaneously, and is not observed experimentally. Displacement of a chlorine atom in chlorobenzene is thermoneutral, could occur, but would not be detected experimentally (unless the Cl atoms were isotopically labeled, denoted as Cl* below). Displacement of bromine and iodine atoms in bromobenzene and iodobenzene are exothermic, can occur spontaneously, and are observed experimentally.

$$Cl + C_6H_5F \rightarrow C_6H_5Cl + F \qquad \Delta H = +128 \text{ kJ mol}^{-1} \tag{5c}$$

$$Cl + C_6H_5Cl^* \rightarrow C_6H_5Cl + Cl^* \qquad \Delta H = 0 \text{ kJ mol}^{-1} \tag{19}$$

$$Cl + C_6H_5Br \rightarrow C_6H_5Cl + Br \qquad \Delta H = -59 \text{ kJ mol}^{-1} \tag{20}$$

$$Cl + C_6H_5I \rightarrow C_6H_5Cl + I \qquad \Delta H = -125 \text{ kJ mol}^{-1} \tag{21}$$

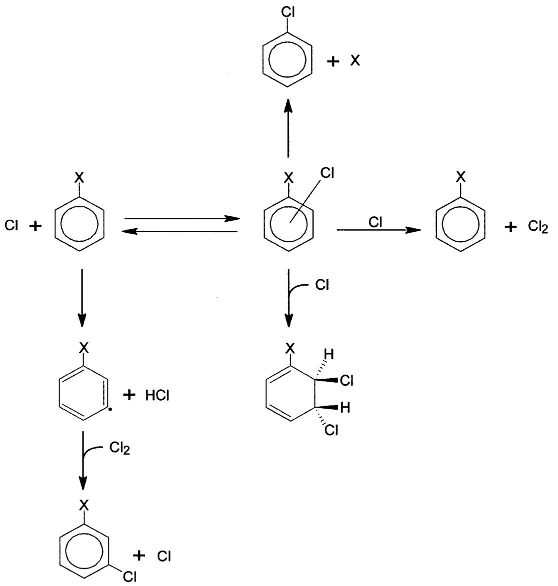


Figure 9. General reaction scheme describing the reaction of Cl atoms with monosubstituted aromatic compounds. For simplicity only one product isomer is shown.

It has been suggested that the displacement reactions 20 and 21 occur via the formation of a $C_6H_5X{-}Cl$ adduct which decomposes to give C_6H_5Cl and X.[4,5] Thermochemical considerations noted above preclude such a fate for the $C_6H_5F{-}Cl$ adduct. On the basis of the considerations given above, we propose that the reactions of Cl atoms with the monohalobenzenes proceed via the general mechanism given in Figure 9 which is a modification of Figure 3 to reflect the possibility of X atom elimination. Hydrogen atom abstraction proceeds with a rate constant of the order of $10^{-17}{-}10^{-16}$ cm^3 molecule^{-1} s^{-1} from C_6H_5X while formation of the $C_6H_5X{-}Cl$ adduct proceeds with a rate constant of the order of 10^{-10} cm^3 molecule^{-1} s^{-1}. The $C_6H_5X{-}Cl$ adduct decomposes rapidly to reform reactants or to give C_6H_5Cl and X atoms. Several interesting predictions arise from the mechanism predicted above. First, it would be predicted that in the reactions of Cl atoms with C_6H_5Br and C_6H_5I the hydrogen atom abstraction channel accounts for approximately $10^{-16}/10^{-11} = 10^{-5}$ of the total reaction at 296 K. Second, the abstraction channel will have a positive temperature dependence while adduct formation will have a negative temperature dependence. Hence, the relative importance of the abstraction channel is expected to increase sharply with increasing temperature. Future studies would be of interest to confirm or refute these predictions.

4.2 Reaction of OH Radicals with C_6H_5F. The value of $k_{10} = (7.9 \pm 2.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} measured herein in 700 Torr of air diluent is indistinguishable from that of $k_{10} = (6.31 \pm 0.81) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} measured in 25−50 Torr of argon.[19] There is no discernible effect of the pressure or nature of the diluent gas on k_{10} over the range studied. From the nonlinear Arrhenius behavior at elevated temperatures, Wallington et al.[19] concluded that at ambient temperature the majority of the reaction of OH radicals with C_6H_5F proceeds to give the $C_6H_5F{-}OH$ adduct which is stable on a time scale of at least 10^{-2} s. The agreement between values of k_{10} measured using the relative rate and flash photolysis methods shows that under the present experimental conditions (700 Torr of air, 296 K) decomposition back to reactants is not an important fate of the $C_6H_5F{-}OH$ adduct. By analogy to the existing database concerning OH-aromatic adducts,[1] it seems likely that the fate of the $C_6H_5F{-}OH$ adduct in the smog chamber experiments and in the atmosphere is reaction with O_2 or NO_2.[1] At ambient temperature and pressure, the OH-aromatic adducts studied to date (benzene-OH, toluene-OH, phenol-OH, *p*-xylene-OH, *m*-xylene-OH, and aniline-OH) react with O_2 and NO_2 with rate constants which lie in the range $(0.2{-}8.0) \times 10^{-14}$ and $(3{-}5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively[1,29−31]. Assuming that the reactivity of the $C_6H_5F{-}OH$ adduct toward O_2 and NO_2 is within the range of those adducts measured previously it follows that $k_{23}/k_{22} = (0.4{-}25) \times 10^3$.

$$C_6H_5F{-}OH + O_2 \rightarrow \text{products} \tag{22}$$

$$C_6H_5F{-}OH + NO_2 \rightarrow \text{products} \tag{23}$$

During the present experiments, the concentration ratio $[O_2]/[NO_2]$ was $(1.5{-}15) \times 10^4$. In polluted urban air, the NO_2 concentration is typically 1−100 ppb, and so the $[O_2]/[NO_2]$ ratio is $(2{-}200) \times 10^6$. Likely, reaction 22 is the dominant fate of the $C_6H_5F{-}OH$ adduct in both the present work and in urban air.

5. Conclusions

The results from the present work and previous studies from our laboratories and elsewhere provide a consistent picture of the kinetics and mechanism of the reaction of Cl atoms and OH radicals with C_6H_5F. Under ambient conditions, both reactions proceed predominantly via the formation of an adduct. The fate of the adducts is however very different. The $C_6H_5F{-}Cl$ adduct decomposes to regenerate the reactants on a time scale which is very short (ca. 10^{-8} s). In contrast, the $C_6H_5F{-}OH$ adduct is stable over a time scale of at least 10^{-2} s.[19] There is little, or no, reaction of the $C_6H_5F{-}Cl$ adduct with O_2 and an upper limit of $k(C_6H_5F{-}Cl + O_2) < 6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} was derived herein. In contrast, assuming behavior similar to that of other aromatic-OH adducts, the $C_6H_5F{-}OH$ adduct is expected to react with O_2 with a rate constant of the order of 10^{-14} cm^3 molecule^{-1} s^{-1}.[1,29−31] The atmospheric chemistry of the $C_6H_5F{-}Cl$ and $C_6H_5F{-}OH$ adducts is very different. It would be interesting to conduct ab initio quantum mechanical studies to provide insight into the fundamental reasons for the different behaviors of the two adducts. Unfortunately, such studies are beyond the scope of the present work. In light of the dramatically different atmospheric fates of the adducts discussed above, reaction 5 is not a suitable candidate for initiating the oxidation of C_6H_5F in smog chamber studies of its atmospheric oxidation mechanism.

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