

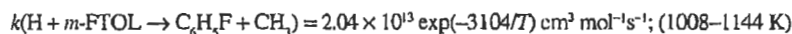
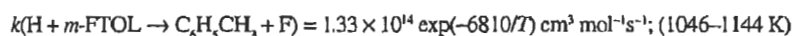
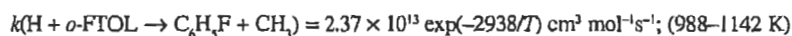
Hydrogen Atom Attack on Fluorotoluenes: Rates of Fluorine Displacement

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Abstract. Rates of hydrogen atom attack on *o*-fluorotoluene (*o*-FTOL) and *m*-fluorotoluene (*m*-FTOL) at temperatures of 988–1144 K and pressures of 2–2.5 bar have been determined in a single-pulse shock tube study. Hydrogen atoms, generated from the decomposition of hexamethylethane, were allowed to react with the substrates and the characteristic products observed. Rate constants for two reaction channels, displacement of fluorine or methyl, were determined relative to displacement of methyl from 1,3,5-trimethylbenzene (135TMB). Evidence is presented that abstraction of F is unimportant over the studied temperature range. With $k(\text{H} + 135\text{TMB} \rightarrow m\text{-xylene} + \text{CH}_3) = 6.7 \times 10^{13} \exp(-3255/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, the following rate expressions have been derived:



Uncertainties in the relative rate constants are estimated to be factors of about 1.1, while the above absolute values have estimated expanded uncertainties of about a factor of 1.4 in rate, 10 kJ mol⁻¹ in the activation energy, and a factor of 3 in the A-factor. The present data are compared with relevant literature data. From our data and the thermochemistry, a model of the elementary steps comprising displacement of F is developed. On the basis of the model fit to our data, rate constants for the addition of atomic fluorine to toluene at 1100 K are derived. Rate expressions for fluorination reactions of toluene are also determined. The significance of the present results is discussed in the context of the formation of fluorinated byproducts in high-temperature systems.

INTRODUCTION

An understanding of the thermal reactions of halocarbons is relevant to the chemistry of flame inhibition^{1,2} and to the destruction of halogenated wastes in municipal and industrial waste incinerators.³⁻⁵ Within the halocarbons, fluorine-containing compounds are a notable sub-class which includes most of the current and proposed alternative refrigerants and fire suppressants, as well as hazardous wastes. Although it is known that incineration of fluorine-containing organics under appropriate conditions leads to the breakdown of the organic backbone and the removal of fluorine, a detailed

understanding of the process does not yet exist. There are presently relatively few experimental data on the rates and mechanisms of the reactions responsible for the removal of fluorine. Such data are critical inputs in fundamental reaction models that are increasingly being used to understand and ultimately control reaction efficiencies and pathways in chemical systems.

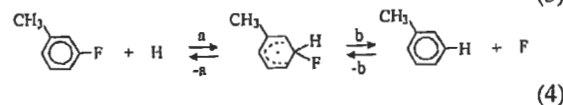
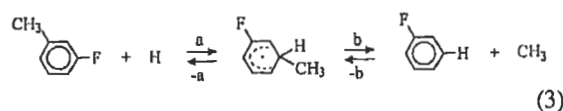
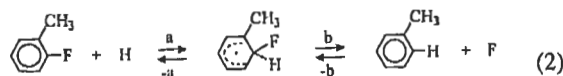
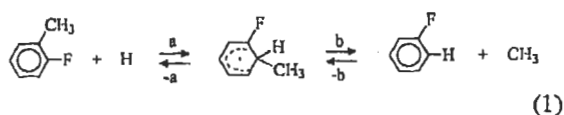
In the combustion of hydrocarbons, abstraction of hydrogen by OH or O is an extremely important reaction. In contrast, abstractions of halogen by oxygen-centered radicals are highly endothermic, so the combustion of halocarbons must proceed either much more

slowly or via other pathways. One of the few alternative routes involves abstraction of halogen by atomic hydrogen, a reaction that is highly exothermic in all cases. Despite the exothermicity of the reaction, we have shown in recent experiments⁶ that hydrogen atoms abstract fluorine only very slowly from saturated organic compounds. This is contrary to some previously accepted reports.^{7,8} Our results also demonstrate that the behavior of fluorine is substantially different from that of the other halogens, which are readily abstractable by atomic hydrogen.

The reactions of atomic hydrogen with unsaturated fluorocarbons at high temperatures have been almost unexplored. The few reports in the literature^{9,10} have indicated that defluorination of fluorobenzenes by atomic hydrogen is a relatively fast reaction at temperatures in the neighborhood of 1000 K. The reaction was postulated to occur via an abstraction mechanism, although the reported rates are at least 200 times faster than allowed by our measured maximum value for F abstraction. Because the previous studies utilized a high-temperature flow system, one possibility is that the observed defluorination was due to wall reactions. Another possibility is that the rate data are correct, but the proposed mechanism is not valid. Our primary aim in the present work was to determine which of the above situations was the case.

We report here the results of a single-pulse shock tube study of the reaction of atomic hydrogen with *ortho*-fluorotoluene (*o*-FTOL) and *meta*-fluorotoluene (*m*-FTOL) at temperatures between 988–1140 K and pressures near 2 bar. Compared with flow systems, an important advantage of the shock tube method is that the reaction time is far shorter than the time required for diffusion of species to the reactor wall. This situation ensures that we have isolated the gas-phase chemistry. A complication of the study is that the reaction of atomic hydrogen with fluorotoluene may occur via more than one pathway. In our system we are able to associate unique products with specific pathways, so we are able to determine rate constants for particular processes rather than simply an overall value.

On the basis of previous studies of hydrogen atom attack on aromatics,^{9–12} the methyl group of fluorotoluenes is expected to be removed via a displacement reaction. This is also a possibility for removal of fluorine from the aromatic structure, leading to the following conceivable reactions:



There are significant differences in the thermochemistry for the above reactions. Displacement of methyl is exothermic by about 45 kJ mol⁻¹ and should therefore readily occur. In the case of fluorine, however, the C–F bond energy at 298 K is about 60 kJ mol⁻¹ greater than that of the C–H bond.¹³ In previous reports of defluorination it was argued on the basis of the endothermicity and the then-accepted rates for fluorine abstraction that the displacement reaction was unimportant. A detailed model of the reaction was not constructed, however. While there is no doubt that hydrogen can add to the fluorine-carrying carbon, the central question is to what extent addition of H will be reversed. The above issue also has bearing on the question of how fluorine is initially released into a reacting system of fluorine-containing aromatics. If ejected as atomic fluorine, various very rapid reactions of F will ensue. In contrast, if released as HF, the exceptional strength of this bond will cause the fluorine to be effectively removed as a reactant except under extremely oxidizing conditions. In this respect fluorine differs from the other halogens, where the HX bond energies are weak enough that reactions of the type R + HX → RH + X can easily re-release halogen atoms into the system.

EXPERIMENTAL

Chemicals

Hydrogen (Matheson, 99.9%) and ultrahigh purity argon (Matheson, 99.999%)¹⁴ were passed through oxygen scrubbers and drying tubes before use. *o*-Fluorotoluene (Aldrich, stated purity 99+%) and *m*-fluorotoluene (Aldrich, 99%) were purified through preparatory gas chromatography to remove small amounts of fluorobenzene and toluene. GC analysis of the resulting material showed no detectable fluorobenzene and only traces of toluene. 1,3,5-Trimethylbenzene (Aldrich, 99+%) was used without further purification. The primary impurities in the 135TMB were other isomers of trimethylbenzene and traces of *m*-xylene. Analytical results for all products were corrected for the background material.

Chromatographic Analysis

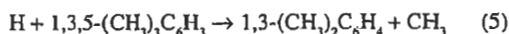
Two gas chromatographs equipped with FID detection were used in the analysis of the reaction mixtures. Light

hydrocarbons ($\leq C_4$) were separated on a 3-m HayeSep N (80-100 mesh) column operated isothermally at 100 °C or 110 °C. Larger components were separated on a 30-m, 0.53-mm-i.d. Restek Rtx-200 column. The column temperature was held at 35 °C for 4 min and then raised to a final temperature of 225 °C at 8 °C/min. Retention times and response factors of the fluorotoluenes, fluorobenzene, toluene, and xylene were determined from samples of these compounds, while the response factor of isobutene was assumed equal to that of 1-butene.

Apparatus and Procedure

Experiments were carried out with a heated single-pulse shock tube. Details of the system have been published previously.^{6,15} In brief, an argon gas mixture containing 200 mL/L H_2 , a few hundred $\mu\text{L/L}$ (ppm) of hexamethylethane (HME), 2-10 mL/L of our standard and the substrate of interest, and a radical inhibitor is placed in the sample side of the shock tube. Rupture of the diaphragm separating the driver and sample side of the shock tube generates the shock wave and results in rapid compression and heating of the gas. In the current experiments, gas temperatures during reaction were in the range of 990-1140 K and pressures in the range of $2-2.5 \times 10^5$ Pa (2-2.5 bar). In the present configuration, the temperature is maintained for about 500 μs before the gas is cooled by expansion. Hydrogen atoms are produced from the thermal decomposition of HME. Competitive reaction of the hydrogen atoms with our standard and the compound of interest generates distinct products for each reaction pathway. These products are analyzed immediately following the shock by utilizing a series of valves and sample loops to admit controlled amounts of the product mixture into the two gas chromatographs.

In the present instance, H atoms are generated from the thermal decomposition of HME, which undergoes the reaction: $\text{HME} \rightarrow 2 \text{ } t\text{-butyl} \rightarrow 2 \text{ } i\text{-C}_4\text{H}_8 + 2\text{H}$. Decomposition of HME is monitored both by formation of isobutene and disappearance of starting material. The extent of HME reaction can be used to determine the temperature of the experiment since the rate expression $k(\text{HME} \rightarrow 2 \text{ } t\text{-butyl}) = 3 \times 10^{16} \times \exp(-34500/T) \text{ s}^{-1}$ has been determined previously.¹⁵ Relative rate constants for reactions of H are determined directly from the ratios of products from H atom attack on the standard and compound of interest. As our standard, we use displacement of methyl from 135TMB:



The rate expression¹² for this reaction, $k(950-1100 \text{ K}) = 6.7 \times 10^{13} \exp(-3255/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, was previously determined relative to the rate of hydrogen abstraction from methane, for which $k(\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2) = 2.4 \times 10^{14} \exp(-7000/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the temperature range of 1000-1200 K.¹⁶

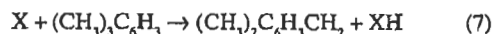
Because of their large excess and thermal stability, the concentrations of 135TMB and fluorotoluene are essentially unchanged over the course of the reaction. The aromatic products of reactions 1-5 are also stable under our conditions. Hence, comparison of the molar amounts of the *m*-xylene (1,3-dimethylbenzene), fluorobenzene, and toluene gives a direct

measure of the relative rates of desubstitution of the respective aromatics. For example, $k_3/k_1 = [m\text{-xylene}][o\text{-FTOL}]/[\text{C}_6\text{H}_5\text{F}][135\text{TMB}]$ and $k_3/k_2 = [m\text{-xylene}][o\text{-FTOL}]/[\text{C}_6\text{H}_5\text{CH}_3][135\text{TMB}]$. The principal experimental problems were traces of toluene and *m*-xylene present in the starting materials. These necessitate small corrections to the analytical results for these compounds. These corrections are negligible except at very low conversions of HME, where they are a limiting factor in the uncertainty of our measurements.

In order to generate more hydrogen atoms at low temperatures, and hence increase the conversion of fluorotoluene and 135TMB to more easily measured values, we added 20% H_2 to our gas mixtures. This has the effect of creating a moderate chain reaction. In the presence of H_2 , radicals such as F and CH_3 can regenerate hydrogen atoms via



As an alternative, they can abstract H from 135TMB or FTOL.



Reactive radicals are thus either converted to H or scavenged by 135TMB or FTOL. The substituted benzyl radicals formed in reactions 7 and 8 are quite stable and do not decompose under our conditions. Because of their large resonance energy, they react only very slowly with closed shell species in our system. The primary fate of these species is recombination with radicals in the system. Such paths will be the primary chain termination steps under our conditions. Consistent with this, small amounts of 1-ethyl-3,5-dimethylbenzene (the product of methyl + 3,5-dimethylbenzyl recombination) were observable at higher degrees of reaction.

Reactions 7 and 8 with $\text{X} = \text{H}$ are ways of removing H atoms from our system without generating a product related to the primary reactions of interest. For attack of H on 135TMB, the ratio of hydrogen abstraction to methyl displacement has been previously determined as $k_{\text{abs}}/k_{\text{disp}} = 5.6 \exp(-1086/T)$,¹² so that $k_{\text{abs}}/k_{\text{disp}} \approx 2$ in the temperature range of our study. A similar ratio is expected for the fluorotoluenes. Abstraction of H from 135TMB or FTOL is expected to be a sink for about 30% of the H atoms generated in our system. This decreases the absolute amounts of our observed products, but otherwise does not affect the results. Since we know from previous studies that each isobutene formed is equivalent to one H atom released into our system, we are able to determine the effect of adding H_2 to our mixtures. The chain length is equal to the ratio of the summed molar amounts of products from H compared with the quantity of isobutene. After a calculated correction for the unobserved products from reactions 7 and 8 with $\text{X} = \text{H}$, we find chain lengths in the range of 2 to 2.5.

RESULTS

Mixtures used in the present experiments are listed in Table 1. The concentrations of HME, 135TMB, and the fluorotoluenes were varied in order to test the correct-

ness of our postulated mechanism. These changes did not affect the relative rates within the experimental uncertainty of about $\pm 10\%$.

The primary products that we observe are isobutene, methane, fluorobenzene, toluene, and *m*-xylene. Isobutene results from decomposition of HME, while the other products stem from hydrogen atom attack on fluorotoluene or 135TMB. We also observe a small amount of propene in our system. As previously discussed,¹⁷ this product arises from isomerization of the *t*-butyl radical via a 1,2 hydrogen atom shift, followed by β -fission of methyl. Consistent with previous results, $C_3H_7/i-C_4H_9 \approx 0.03$. This minor channel is included in calculations of the overall rate of HME decomposition. Methane clearly stems from the methyl radicals produced in reactions 1, 3, and 5. In the present system most methyl radicals abstract hydrogen from H_2 or 135TMB to form methane. Traces of ethane and 3,5-dimethylethylbenzene were also observed and can be attributed to recombination of methyl with itself or the radical product of reaction 7.

Desubstitution reactions of the parent benzenes are responsible for the fluorobenzene, toluene, and *m*-xylene that we observe. Figure 1 shows Arrhenius-type plots of k_2/k_1 and k_5/k_3 , the relative rate constants for displacement of methyl from 135TMB and the isomeric fluorotoluenes. The following rate expressions are obtained:

$$\log(k_2/k_1) = (0.451 \pm 0.05) + (-138 \pm 49)/T; (988-1142 \text{ K})$$

$$\log(k_5/k_3) = (0.516 \pm 0.10) + (-65 \pm 106)/T; (1008-1144 \text{ K})$$

The above-listed uncertainties are $\pm \sigma$ and are a measure of precision only. It is well known that the most important experimental uncertainties are often systematic. Uncertainties in comparative rate measurements of the present type have been discussed previously in detail.¹⁵ Overall, we estimate that the relative rate constants should be accurate to within $\pm 10\%$, while the estimated uncertainty in the relative activation energies is about 5 kJ mol⁻¹. Relative to the standard reaction of displacement of methyl from 135TMB, for which $k_3 = 6.7 \times 10^{13} \text{ exp}(-3255/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,¹² we obtain:

$$k_1 = 2.37 \times 10^{13} \text{ exp}(-2938/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}; (988-1142 \text{ K})$$

$$k_3 = 2.04 \times 10^{13} \text{ exp}(-3104/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}; (1008-1144 \text{ K})$$

Taking into account the uncertainties in the parameters for the standard reaction, the measurement, and possible systematic errors, the expanded uncertainties in the absolute parameters are estimated to be about a factor of 1.4 in rate, 10 kJ mol⁻¹ in the activation energy, and a factor of 3 in the A-factor. The above parameters are listed to a greater degree of exactness so that information on the relative values of the rate constants is not lost due to rounding.

The toluene that we observe must arise through defluorination reactions. The only other likely source is demethylation of the *m*-xylene formed in reaction 5. We can safely assume, however, that the rate constant for the reaction $H + m\text{-xylene} \rightarrow C_6H_5CH_3 + CH_3$ is about two-thirds that of reaction 5. Given this and the large excess of 135TMB and fluorotoluene, it is easily shown that the above reaction makes a negligible contribution to the toluene product flux. This is further confirmed by the equality of the rate constants obtained with mixtures of different starting concentrations. It is clear, therefore, that hydrogen atom attack is able to remove fluorine from the aromatic ring. As we will show, defluorination is occurring through displacement reactions 2 and 4. The defluorination reaction is a factor of 4-7 slower than demethylation. Because of this and the greater quantity of toluene impurity in the starting mixture, we were unable to obtain reliable rate data on the defluorination reaction at the lowest temperatures of our study. Results are presented in Fig. 2. For the relative rates we find:

$$\log(k_3/k_2) = (-0.097 \pm 0.09) + (1210 \pm 97)/T; (1012-1142 \text{ K})$$

$$\log(k_5/k_4) = (-0.299 \pm 0.25) + (1544 \pm 268)/T; (1046-1144 \text{ K})$$

With k_3 as before, these lead to the following absolute rates:

$$k_2 = 8.38 \times 10^{13} \text{ exp}(-6041/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}; (1012-1142 \text{ K})$$

$$k_4 = 1.33 \times 10^{14} \text{ exp}(-6810/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}; (1046-1144 \text{ K})$$

Table 1. List of the mixtures used in the present investigations

Mixture	Components ^a
A	129 $\mu\text{L/L}$ HME; 2.1 mL/L 135TMB, 5.1 mL/L <i>m</i> -FTOL; 200 mL/L H_2 , in argon
B	157 $\mu\text{L/L}$ HME; 6.7 mL/L 135TMB, 10 mL/L <i>m</i> -FTOL; 200 mL/L H_2 , in argon
C	118 $\mu\text{L/L}$ HME; 3.8 mL/L 135TMB, 9.2 mL/L <i>o</i> -FTOL; 200 mL/L H_2 , in argon
D	190 $\mu\text{L/L}$ HME; 2.2 mL/L 135TMB, 3.3 mL/L <i>o</i> -FTOL; 200 mL/L H_2 , in argon

^aHME = hexamethylethane; 135TMB = 1,3,5-trimethylbenzene; *m*-FTOL = *meta*-fluorotoluene; *o*-FTOL = *ortho*-fluorotoluene.

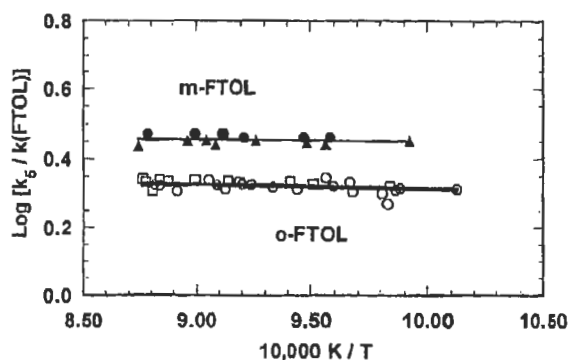


Fig. 1. Rate constant for displacement of methyl from *ortho*- and *meta*-fluorotoluenes by atomic hydrogen relative to that for displacement of methyl from 135-TMB. Filled symbols: *m*-fluorotoluene; triangles mixture A, circles mixture B. Unfilled symbols: *o*-fluorotoluene; squares, mixture C; circles, mixture D.

Expanded uncertainties in the absolute rate constants should be similar to those indicated earlier, about 1.4 in rate, 10 kJ mol⁻¹ in the activation energy, and a factor of 3 in the A-factor.

DISCUSSION

The results presented above show that both fluorine and methyl groups are removed by hydrogen atom attack on fluorotoluenes. Although our primary interest is the reaction responsible for removal of fluorine, in the following section we will briefly compare the available data on demethylation of substituted benzenes. Thereafter we will discuss the results on defluorination.

Displacement of Methyl by Atomic Hydrogen

Demethylation of aromatic compounds by H atom attack is known to occur via a displacement mechanism. For *o,m*-fluorotoluenes the reaction is exothermic by more than 40 kJ mol⁻¹. Our data show that methyl is displaced from the *ortho* isomer about 30% faster than from the *meta*. Since it is well established that H atom addition to a methyl site is nearly irreversible,^{9,11} this rate difference reflects a small difference in the rate constant for addition of H. Table 2 compares reported rate constants for displacement of methyl groups from several substituted benzenes. On a per-methyl basis only small rate differences are observed, with the most labile compound, *o*-FTOL, reacting only about 40% faster than the slowest at 1000 K. It is interesting that the most reactive compound has a substituent *ortho* to the methyl group that is removed. In comparing the present results with other data on displacement reactions from

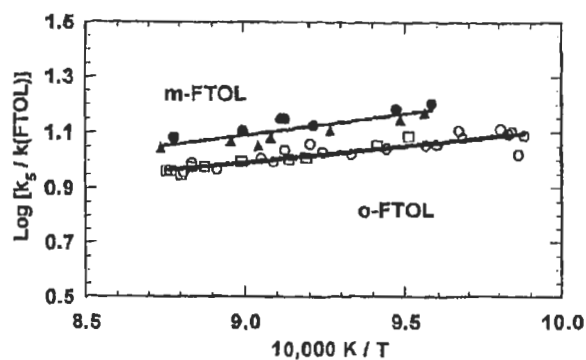


Fig. 2. Rate constant for displacement of fluorine from *ortho*- and *meta*-fluorotoluenes by atomic hydrogen relative to that for displacement of methyl from 135-TMB. Filled symbols: *m*-fluorotoluene; triangles mixture A, circles mixture B. Unfilled symbols: *o*-fluorotoluene; squares, mixture C; circles, mixture D.

aromatics it is seen that this is a general trend regardless of the group that is removed. That is, *ortho* substitution appears to speed up the reaction. Although this is probably indicative of a steric effect, the situation is expected to be more complicated and there are indications^{9,12} that polar effects are also important.

In the studies of demethylation, only the toluene system has been investigated by more than one group. The reported rate constants (Table 2) are in excellent agreement, except for small differences in the measured activation energies. The lower temperature data point of Baldwin et al.¹⁸ is more compatible with the higher of the reported activation energies. Tsang et al.¹² have also pointed out that since 135TMB and toluene react with near identical rates on a per-methyl basis, it is unlikely that the activation energies for these compounds are as different as the measurements suggest. Although there is some small variation in the reported pre-exponential factors, the A-factors for methyl displacement are equal within the experimental uncertainties.

Displacement of Fluorine by Atomic Hydrogen

Our data show that attack of hydrogen atom removes fluorine from the aromatic ring, albeit four to seven times slower than displacement of methyl. The measured rate constants are similar to those reported previously for fluorobenzene⁹ and *o,m*-chlorofluorobenzenes.¹⁰ In the earlier studies it was suggested that the mechanism of defluorination involved direct abstraction of F. If occurring in the present system, abstraction of F would lead to a methyl-substituted phenyl radical which could then abstract hydrogen from H₂ or 135TMB and thereby form toluene. Since this is the same product

Table 2. Reported rate constants for some reactions of F and H with aromatics and related compounds

Reaction	Rate expression cm ³ mol ⁻¹ s ⁻¹ (Temp)	Rate constant cm ³ mol ⁻¹ s ⁻¹ (Temp/K)	Reference
<i>Displacement of methyl from aromatics</i>			
H + C ₆ H ₅ CH ₃ → C ₆ H ₆ + CH ₃	1.2 × 10 ¹³ exp(-2578/T) [950–1100 K] 1.5 × 10 ¹³ exp(-2914/T) [931–1039 K] 3 × 10 ¹¹ [773 K]	9.1 × 10 ¹¹ (1000) 8.1 × 10 ¹¹ (1000) –	11 9 18
Fit to all data	2.8 × 10 ¹³ exp(-3462/T) [773–1100K]	8.8 × 10 ¹¹ (1000)	
H + 135TMB → <i>m</i> -xylene + CH ₃	6.7 × 10 ¹³ exp(-3255/T) [980–1120 K]	2.6 × 10 ¹² (1000)	12
H + <i>p</i> -ClTOL → C ₆ H ₅ Cl + CH ₃	3.5 × 10 ¹³ exp(-3710/T) [980–1120 K]	8.6 × 10 ¹¹ (1000)	19
H + <i>o</i> -FTOL → C ₆ H ₅ F + CH ₃	2.37 × 10 ¹³ exp(-2938/T) [988–1142 K]	1.2 × 10 ¹² (1000)	This work
H + <i>m</i> -FTOL → C ₆ H ₅ F + CH ₃	2.04 × 10 ¹³ exp(-3104/T) [1008–1144 K]	9.0 × 10 ¹¹ (1000)	This work
<i>Displacement of fluorine by H</i>			
(H + C ₆ H ₅ F → C ₆ H ₆ + F) ^a	2.0 × 10 ¹³ exp(-5066/T) [918–1001 K]	1.3 × 10 ¹¹ (1000)	9
H + <i>o</i> -FTOL → C ₆ H ₅ CH ₃ + F	8.38 × 10 ¹³ exp(-6041/T) [1012–1142 K]	2.0 × 10 ¹¹ (1000)	This work
H + <i>m</i> -FTOL → C ₆ H ₅ CH ₃ + F	1.33 × 10 ¹⁴ exp(-6810/T) [1046–1144 K]	1.4 × 10 ¹¹ (1000)	This work
H + <i>o</i> -C ₆ H ₄ FCl → C ₆ H ₅ Cl + F	–	1.1 × 10 ¹¹ (1000)	10
H + <i>m</i> -C ₆ H ₄ FCl → C ₆ H ₅ Cl + F	–	1.0 × 10 ¹¹ (1000)	10
<i>Reactions of F</i>			
F + C ₃ H ₆ → C ₃ H ₅ F + CH ₃	–	1.35 × 10 ¹³ (298) ^b	20
F + C ₃ F ₆ → C ₃ F ₇	–	1.4 × 10 ¹³ (273) ^c	22
F + C ₂ H ₄ → Products	–	1.6 × 10 ¹⁴ (298)	24
F + C ₆ H ₅ CH ₃ → H + <i>o</i> -FTOL	2.3 × 10 ¹³ exp(+520/T) [1012–1142K] ^d	3.9 × 10 ¹³ (1000)	This work
F + C ₆ H ₅ CH ₃ → H + <i>m</i> -FTOL	3.7 × 10 ¹³ exp(-90/T) [1046–1144K] ^d	3.4 × 10 ¹³ (1000)	This work
F + C ₆ H ₅ CH ₃ → C ₆ H ₅ F + CH ₃	–	8.0 × 10 ¹² (296)	25
F + C ₆ H ₅ CH ₃ → F-C ₆ H ₄ CH ₃ + H	–	2.0 × 10 ¹³ (296)	25
F + C ₆ H ₅ CH ₃ → F-C ₆ H ₅ CH ₃	–	1.08 × 10 ¹⁴ (298)	26
F + C ₆ H ₆ → C ₆ H ₅ F + H	–	2.4 × 10 ¹³ (296)	25

^aThe mechanism was originally suggested to be abstraction of F. ^bBased on reported relative rate and k_{298} (F + C₃H₆ → Products) = 2.7 × 10¹³ cm³ mol⁻¹ s⁻¹ from ref 21. ^cBased on reported relative rate and k_{273} (F + CH₄ → CH₃ + HF) = 4.2 × 10¹³ cm³ mol⁻¹ s⁻¹ from ref 23. ^dCalculated from detailed balance and the reverse rate constant.

formed in the displacement reaction, we cannot directly distinguish the two mechanisms solely on the basis of the present experimental data. However, in recent work⁶ we have demonstrated that hydrogen atoms abstract fluorine only very slowly from a fluorinated aliphatic. Fluorine abstraction from aromatics should be even slower because the C–F bonds in aromatics will in general be stronger than those of aliphatics. Based on our previous maximum rate constant for fluorine abstraction at 1100 K, $k(\text{RF} + \text{H} \rightarrow \text{R} + \text{HF}) \leq 1.6 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, abstraction of fluorine must be contributing less than 1% to our measured overall rate. The data of Kochubei and Moin²⁷ on H + CF₄ and theoretical calculations²⁸ suggest that fluorine abstraction is even less important. The above evidence is circumstantial, but we believe it to be compelling. We know of no instance in the literature, for instance, where the gas phase abstraction of an atom from an aromatic compound is faster than from a comparable aliphatic, and certainly not by the orders of magnitude that would be required to explain the present

results.

The most reasonable alternatives to abstraction are either a direct route or displacement. Direct routes such as C–F bond fission or elimination of HF are ruled out by the very high activation energies that would be required. This is further confirmed by the experimental observation that the amount of toluene product was dependent on the quantity of HME and the ratio of 135TMB/FTOL, but not on the absolute starting concentration of fluorotoluene. Displacement of F by H is endothermic by about 55 kJ mol⁻¹ at 1000 K¹³ and has previously^{9,10} been ruled out on this basis. However, as we will show, if the barrier to fluorine addition is low, all of the data can be accounted for by a displacement model. The reactions of F with toluene^{25,26} and benzene²⁵ have recently been studied near ambient temperature. Although the measured rates of the F + toluene reaction differ by about a factor of five (see Table 2), there is general agreement that the addition reaction is very fast. The observed rates indicate that the barrier to F addition

must be less than about 8 kJ mol⁻¹. In the following section we develop a model which shows that the defluorination results for fluorobenzenes can be interpreted in terms of a displacement mechanism where loss of F or H from the substituted cyclohexadienyl radical intermediate is a competitive process.

Displacement Model of Defluorination

Assuming a displacement mechanism, what we have measured is the overall rate constant, given in the case of *o*-FTOL by $k_2 = k_{2a}k_{2b}/(k_{-2a} + k_{2b})$. To demonstrate the viability of a displacement mechanism, we have fit our rate data using a set of rate constants consistent with the thermochemistry and what is currently known about rates of addition of H and F to aromatic compounds. Our calculations suggest that under our experimental conditions pressure effects on k_2 and k_4 should be small, so we have neglected any small corrections that could result from chemical activation processes. The comparison using high pressure rate parameters is shown in Fig. 3. The thermodynamic properties of the compounds and the final rate expressions are given in Tables 3 and 4. Although the parameters of Table 4 are not a unique set, acceptable values are constrained both by the thermochemistry and the available kinetic information on rates of addition of H and F to aromatic compounds. These constraints are discussed below.

Thermochemistry. Of the fluorotoluenes, an experimental enthalpy of formation is available only for the para isomer, with $\Delta H_{f,298}(p\text{-FTOL}) = -147.5 \pm 1.2$ kJ mol⁻¹.²⁹ Values for the ortho and meta compounds should be similar and have been estimated by Liebmann and coworkers³⁰ as $\Delta H_{f,298}(o\text{-FTOL}) = -149$ kJ mol⁻¹ and $\Delta H_{f,298}(m\text{-FTOL}) = -150$ kJ mol⁻¹. Enthalpy values calculated by AM1 methods³¹ are incompatible with both the experimental data and group additivity methods and must be considered unreliable. We have adjusted the values of Liebmann and coworkers at 298 K to 1000 K using the thermodynamic functions calculated by Lichanot and Pouchan.³¹ The well-known thermodynamic properties of H, F, and toluene were taken from the TRC Tables¹³ and are similar to those listed by other sources. Estimates of the properties of the substituted cyclohexadienyl intermediates were made by applying corrections to the thermofunctions of the fluorotoluenes. The corrections were initially made on the basis of a comparison of the properties of benzene¹³ and cyclohexadienyl,³² and then further refined by slight adjustment of the frequencies associated with the CCF modes of the radical. The thermodynamic properties of this intermediate are the most uncertain, but although the choices here affect the absolute values of k_{-2a} and k_{2b} , the ratio of k_{-2a}/k_{2b} is unchanged. Hence the calculated

value of the overall rate constant is not affected by the properties of this intermediate. Note that this also means that the present experiments cannot be used to obtain any information about this species.

Kinetic Parameters. To solve for k_2 , we need to know the values of k_{2a} and the ratio k_{-2a}/k_{2b} . The kinetic parameters in the model for the addition of H and F must be compatible with other data on such reactions. For addition of hydrogen atoms to substituted aromatics, data on a variety of compounds³³⁻³⁵ suggest that the A_{2a} factor should lie in the range of 1.5 × 10¹⁰ cm³ mol⁻¹ s⁻¹. In our model, we have fixed the value of A_{2a} at 2 × 10¹⁰ cm³ mol⁻¹ s⁻¹. On the basis of low temperature results with ethene³³ and fluoroethenes,³⁴ it is anticipated that the activation energy for addition of H to the fluorine-carrying carbon of fluorotoluene will be slightly greater than that for the addition to a C-H site of benzene. The minimum value of E_{2a} was therefore set to that reported for addition of H to benzene, 18 kJ mol⁻¹, but otherwise allowed to vary. It is further obvious that $k_{-2a} > k_{2b}$, which limits the maximum allowable value of E_{2b} . Loss of F from the substituted cyclohexadienyl radical, reaction 2b, is related through the thermochemistry to addition of F, reaction -2b. We have restricted the rate parameters for k_{-2b} to be compatible with the low temperature data on the reaction of F with benzene and toluene. Eberhart et al.²⁵ have reported on $F + C_6H_6 \rightarrow FC_6H_5 + H$ and $F + C_6H_5 \rightarrow C_6H_4F + H$ (see Table 2). Their low pressure rates for displacement of H should be close to the high pressure rate for addition of F. Adjusted for statistical factors, their rate constants for displacement of H from benzene and toluene are identical, suggesting

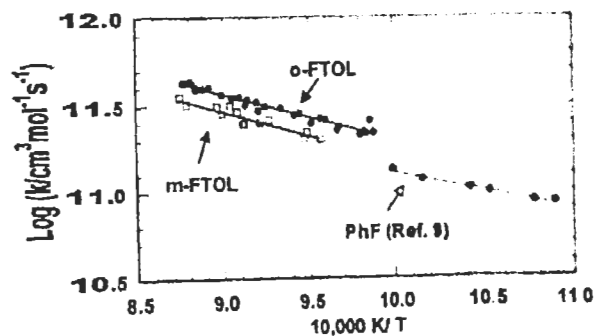


Fig. 3. Rate constants for defluorination of some fluorobenzenes. Data on *ortho* and *meta* fluorotoluene are from this work; data on fluorobenzene are from ref. 9. Solid lines: results of model using the parameters of Table 4. Dashed line: rate expression from ref. 9.

Table 3. Thermodynamic properties of species^a in model. Units of ΔH_f and S are kJ mol^{-1} and $\text{J mol}^{-1} \text{K}^{-1}$. Data are from refs 13, 30, 31, and 32 as discussed in text

Property	Reaction						$\Delta_f X(1000 \text{ K})$
	H	+ <i>o</i> -FTOL	\rightarrow	<i>o</i> -C ₇ H ₈ F	\rightarrow	C ₆ H ₅ CH ₃ + F	
$\Delta H_f(1000 \text{ K})$	222.3	-169.9		-56.9		24.53 82.4	54.6
$S(1000 \text{ K})$	139.9	577.9		615		543.1 185.4	10.7
Property	H	+ <i>m</i> -FTOL	\rightarrow	<i>m</i> -C ₇ H ₈ F	TOL + F	$\Delta_f X(1000 \text{ K})$	
	$\Delta H_f(1000 \text{ K})$	222.3	-171.1		-58.1		24.53 82.4
$S(1000 \text{ K})$	139.9	578.2		615	543.1 185.4	10.4	

^a *o*-FTOL = *o*-fluorotoluene; *o*-C₇H₈F = 6-fluoro-1-methylcyclohexa-2,4-dienyl; *m*-FTOL = *m*-fluorotoluene; *m*-C₇H₈F = 6-fluoro-2-methylcyclohexa-2,4-dienyl.

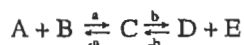
Table 4. Rate parameters from displacement model of defluorination

Reaction ^a	Rate parameters / $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$
k_{2a} H + <i>o</i> -FTOL \rightarrow <i>o</i> -C ₇ H ₈ F	$2.0 \times 10^{13} \exp(-2650/T)$
k_{-2a} <i>o</i> -C ₇ H ₈ F \rightarrow H + <i>o</i> -FTOL	$2.0 \times 10^{13} \exp(-14790/T)$
k_{2b} <i>o</i> -C ₇ H ₈ F \rightarrow C ₆ H ₅ CH ₃ + F	$2.2 \times 10^{14} \exp(-18944/T)$
k_{-2b} C ₆ H ₅ CH ₃ + F \rightarrow <i>o</i> -C ₇ H ₈ F	$5.8 \times 10^{13} \exp(-240/T)$
k_2 H + <i>o</i> -FTOL \rightarrow C ₆ H ₅ CH ₃ + F	$8.4 \times 10^{13} \exp(-6041/T)$
k_{4a} H + <i>m</i> -FTOL \rightarrow <i>m</i> -C ₇ H ₈ F	$2.0 \times 10^{13} \exp(-2170/T)$
k_{-4a} <i>m</i> -C ₇ H ₈ F \rightarrow H + <i>m</i> -FTOL	$2.2 \times 10^{13} \exp(-14310/T)$
k_{4b} <i>m</i> -C ₇ H ₈ F \rightarrow C ₆ H ₅ CH ₃ + F	$1.7 \times 10^{14} \exp(-19019/T)$
k_{-4b} C ₆ H ₅ CH ₃ + F \rightarrow <i>m</i> -C ₇ H ₈ F	$4.6 \times 10^{13} \exp(-170/T)$
k_4 H + <i>m</i> -FTOL \rightarrow C ₆ H ₅ CH ₃ + F	$9.6 \times 10^{13} \exp(-6448/T)$

^a *o*-FTOL = *o*-fluorotoluene; *o*-C₇H₈F = 6-fluoro-1-methylcyclohexa-2,4-dienyl; *m*-FTOL = *m*-fluorotoluene; *m*-C₇H₈F = 6-fluoro-2-methylcyclohexa-2,4-dienyl.

there is little discrimination between the various sites. Their data thus lead to $k_{-2b}(296 \text{ K}) = 8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The data of Markert and Pagsberg²⁶ on F + C₆H₅CH₃ \rightarrow F-C₆H₅CH₃ lead to a significantly larger rate constant, $k_{-2b}(298 \text{ K}) \approx 4.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Since the reason for the discrepancy is not clear, we have forced our rate expression for addition of F to pass through the average of these values, $k_{-2b}(298 \text{ K}) \approx 2.6 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Discussion of Model. It is clear from Table 4 and Fig. 3 that the rate data for defluorination can be fit very well assuming a displacement mechanism. We note that for a general endothermic reaction of the type



the overall rate constant k will be very sensitive to the sum of the overall reaction endothermicity and E_{-b} . In the presently relevant instance, where the reaction rate in the direction D + E \rightarrow A + B is negligible, $k = k_a k_b / (k_{-a} + k_b)$. The activation energy for the overall process will depend on the relative values of k_{-a} and k_b , and must lie

between those of the two extreme situations where $k_b \gg k_{-a}$, and $k_b \ll k_{-a}$. In the former case, almost all additions result in desubstitution, and the measured rate constant and activation energy will pertain to the addition reaction, k_a . This is the situation for displacement of methyl. In the case where $k_b \ll k_{-a}$, the measured rate constant is given by $k_b k_a$ and the overall activation energy will be equal to the sum of the reaction endothermicity and E_{-b} .

The situation for fluorine appears to be intermediate. The fraction of the H addition reactions that result in defluorination is given by the ratio $k_b / (k_{-a} + k_b)$. Our modeled values are in the range of 0.15 to 0.3 for *m*-FTOL and *o*-FTOL. In this regime where k_b and k_{-a} are similar, the value of the ratio $k_b / (k_{-a} + k_b)$ is very dependent on the precise reaction thermochemistry, with differences of even a few kJ mol^{-1} resulting in substantial differences. The exact value is therefore expected to vary from substrate to substrate. Because of this it is uncertain if the faster defluorination rate of *o*-FTOL compared with *m*-FTOL is a reflection of a faster rate of hydrogen atom addition or whether it results from changes in the reaction thermochemistry.

Kinetics of Fluorine Atom Addition to Toluene

The rate expressions for the elementary steps are constrained as discussed above. While we lack enough information for a unique solution, this is enough information to set limits on the rate constants for certain reactions. The rate constant for addition of fluorine to the ortho site of toluene, k_{-2b} , is related through the thermochemistry to k_{2b} and hence to the overall rate of defluorination. Assuming a 5 kJ mol⁻¹ uncertainty in the enthalpy of formation of *o*-FTOL, a 40% uncertainty in our absolute rate constant, and the uncertainty in k_{2b} as discussed in that section, we find that we cannot fit our data unless $k_{-2b}(1100\text{ K}) \geq 2 \times 10^{13}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$. We find a best fit of

$$k_{-2b}(1100\text{ K}) = 4.6 \times 10^{13}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

As discussed in the previous section, an approximate value of this rate constant at room temperature can be derived as $k_{-2b}(296\text{ K}) = (2.6 \pm 2) \times 10^{13}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$. Combined with the data of the present study, this would indicate a small increase in the rate constant from 296 K to 1100 K. If forced to an Arrhenius format, we obtain

$$k_{-2b} \approx 5.8 \times 10^{13}\text{ exp}(-240/T)\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

The above expression is of course dependent on the accuracy of the various experiments. Within the combined experimental uncertainties, a temperature independent value of the rate constant could also be used. In the sense that it is more difficult to fit our measured activation energies with a strictly temperature-independent model, the present data are more in line with the presence of a small barrier. As far as we know, there are no other high temperature results with which to compare our result, or even any low temperature studies which report the activation energy for addition of F to any compound.

The derived rate parameters for fluorine atom addition to the meta position of toluene are similar to those for the ortho site. For *m*-FTOL, however, we were unable to exactly fit our measured activation energy without making small adjustments to either $\Delta H_{f,298}(m\text{-FTOL})$ or E_{-4b} or allowing the barrier to H atom addition to drop below 18 kJ mol⁻¹. Although there is clearly room for the necessary adjustments to $\Delta H_{f,298}(m\text{-FTOL})$ or E_{-4b} , the discrepancy could as easily be accounted for by the overall uncertainty of about 10 kJ mol⁻¹ in our measurement of E_4 . Since it is not clear which is the most likely explanation, we have not adjusted any of the "fixed" parameters and report only the modeled rate expressions. We find "best" fits of

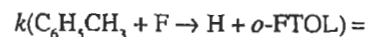
$$k_{-4b}(1100\text{ K}) = 4.0 \times 10^{13}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

$$k_{-4b} \approx 4.6 \times 10^{13}\text{ exp}(-170/T)\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

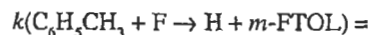
As indicated, the above values are very sensitive to the thermochemistry. For instance, lowering $\Delta H_{f,298}(m\text{-FTOL})$ from -150 kJ mol⁻¹ to -152.4 kJ mol⁻¹ would allow us to fit our measured E_4 and would result in values of k_{-2b} and k_{-4b} that are identical. Although this may suggest that such thermochemistry is preferable, the uncertainties in our measurement of E_4 preclude any firm conclusions.

Kinetics of Fluorination

From the thermochemistry and our measured rate constants for defluorination, we can calculate the rate constants for the fluorination of toluene. From detailed balance, at 1000 K we obtain:



$$2.3 \times 10^{13}\text{ exp}(+520/T)\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$



$$3.7 \times 10^{13}\text{ exp}(-90/T)\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$$

To the extent that the thermochemistry is correct, the uncertainty in these rate expressions should be similar to those of our primary measurements. Notice that these rate constants are much larger than those for high temperature chlorination¹⁹ via a displacement mechanism. The faster rate for fluorination is in large part due to the shift in the energetics of the halogenation reaction from endothermic to highly exothermic. After adjustment for statistical factors, parameters similar to the above would be expected for the displacement of hydrogen by F from other aromatic hydrocarbons. It should be noted, however, that fluorination becomes energetically less favorable as the starting aromatic becomes more fluorinated. Thus, at 1000 K, fluorination of pentafluorobenzene, $\text{C}_6\text{HF}_5 + \text{F} \rightarrow \text{C}_6\text{F}_6 + \text{H}$, is only 5 kJ mol⁻¹ exothermic in comparison with 54 kJ mol⁻¹ for fluorination of benzene.¹³ Such a shift will substantially change the ratio of hydrogen to fluorine loss from the fluorocyclohexadienyl intermediate. In the absence of further data it is not possible to estimate the rate constants precisely. Barring extreme changes in the barriers to addition of H and F, however, it is expected that fluorination of highly fluorinated aromatics will be considerably slower than for the analogous hydrocarbons.

Fluorination Reactions in High Temperature Systems

The displacement reaction of fluorine by atomic hydrogen is expected to be important in a variety of high temperature systems where fluorinated aromatics are present. One consequence of a displacement as opposed

to abstraction mechanism for the defluorination reaction is that the fluorine is initially released as free F atoms instead of HF. If released as HF, the fluorine would effectively be removed from the reacting system because of the exceptional strength of the HF bond. When released as free atomic fluorine, however, the displaced fluorine will be able to migrate to other structures. Because some fluorinated compounds are highly toxic, this is of concern in high temperature systems designed for disposal of hazardous wastes. Notice that the derived rate constants for fluorination of aromatics have magnitudes similar to those expected for abstraction of hydrogen from saturated hydrocarbons. This suggests that one important parameter controlling fluorinated byproduct formation will be the nature and size of the H/F ratio in the organic fraction. With regard to fluorination of products of incomplete combustion (PICs), which are generally unsaturated species, an as yet unresolved issue is the rate constant for hydrogen abstraction by F from sp^2 hybridized carbon. High temperature data regarding this issue are absent and the low temperature data are contradictory, with some workers³⁸ proposing hydrogen abstraction to be substantial, and others²⁵ suggesting it to be relatively unimportant. It is the relative rate of abstraction to displacement for such species that will in part determine to what extent PICs can be fluorinated under conditions of partial combustion. Because of the expected variation of the fluorination rate with the reaction thermochemistry, the fluorine content of the attacked species will also be an important parameter. A firm grasp of the above issues will be required to correctly predict and model the distribution of fluorinated species in high temperature systems.

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