Structure and Reactivity of Protonated α, α, α -Trifluorotoluene in the Gas Phase. A Combined FT-ICR, Radiolytic, and ab Initio MO Study

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The protonation of $CF_3C_6H_5$ and deprotonation of $[CF_3C_6H_5]H^+$ ions have been studied by FT-ICR with the kinetic bracketing technique. The protonation by weak BH⁺ acids is dissociative, with an onset for C_6H_5 - CF_2^+ and HF formation at a gas phase basicity of B equal to 172 kcal mol⁻¹. Stronger acids, CH_5^+ , SO_2H^+ and $C_2H_5^+$ yield persistent $[CF_3C_6H_5]H^+$ ions. These results have been interpreted with the aid of ab initio MO calculations showing that the fluorine atoms have a higher proton affinity than the ring carbons. The dissociative proton transfer appears to be entropically driven, surmounting a $C_6H_5CF_2^+/HF$ binding energy of 10.3 kcal mol⁻¹. The kinetics of proton transfer from $[CF_3C_6H_5]H^+$ to benzene and to $(C_2H_5O)_2CO$, a fairly strong base in the gas phase, show similar rate ratios in FT-ICR and in radiolytic systems at atmospheric pressure.

Introduction

The gas phase reactivity of fluorinated ions and neutrals is directed by the strong electronic effects exerted by fluorine as substituent and by the distinct behavior of fluorine itself when acting as reaction site.^{1,2} Several studies have reported on the protonation of fluoro- and poly(fluorobenzene)s, where the number and relative position of fluorine atoms modulates the relative proton affinities (PA).^{3–12} Recent detailed studies have focussed on unimolecular fragmentation processes involving loss of HF from protonated fluorobenzene.³⁻⁵ To date, no information is available concerning the protonation of a closely related molecule, α, α, α -trifluorotoluene, apart from computational data on the proton affinity of m- and p-positions by semiempirical MNDO and STO-3G ab initio methods.^{13,14} Our interest in the protonation of CF₃C₆H₅ stems from previous studies on the reactivity of gaseous CF₃⁺ ions,¹⁵ powerful electrophilic species vielding ion-molecule adduct ions destabilized by the electronic effect exerted by the CF₃ group and prone to undergo, whenever possible, HF elimination processes. The major product channel from the CF₃⁺ reaction with benzene under mass spectrometric conditions is reported to give C₆H₅CF₂⁺ as ionic product, suggested to arise from CF_3^+ addition to a ring carbon followed by HF elimination¹⁶ (eq 1a). The same reaction evolves into

neutral substitution products when allowed to occur in CF₄ at 1 atm,^{15a,b,d,n} using the radiolytic technique.¹⁷ Such diverse behavior is explained by the fact that the high exothermicity of the CF₃⁺ addition process, estimated to be of the order of 60

kcal mol^{-1,15a} yields excited adduct ions. Their excess energy content may be dispersed either by the unimolecular fragmentation of HF occurring under mass spectrometric conditions (eq 1a) or by efficient collisional quenching with CF₄ at atmospheric pressure. Only in the latter case, pertaining to radiolytic experiments, are persistent $[CF_3C_6H_5]H^+$ ions formed and allowed to evolve by deprotonation into neutral products (eq 1b). The same intermediate ions can in principle be obtained by protonation of CF₃C₆H₅, which may provide information regarding the thermodynamically favored protonation site(s), the possible interconversion between protonated isomers, and relative ease of HF loss, the kinetic features of intermolecular proton transfer. The present study has provided an answer to some of these questions.

Experimental Section

Materials. CH₄, CF₄, C₃H₈, NO, and O₂ were research grade gases from Matheson Gas Products or Union Carbide with stated purity in excess of 99.99%. Aldrich Chemical Co. supplied all other products, except [$^{12}C_6$]benzene (99.9 at.% ^{12}C) which was purchased from Cambridge Isotope Laboratories.

ICR Experiments. The experiments were performed using a Bruker Spectrospin Apex TM 47e spectrometer equipped with an external ion source and a cylindrical (60 mm diameter) "infinity" cell situated between the poles of a 4.7 T superconducting magnet. This instrumental configuration allows the generation of protonated species in the external ion source and their reaction to occur in the cell, where only one neutral component is present. In this way, the kinetics of proton transfer reactions involving a series of selected bases (B) were analyzed in the absence of back reaction. Bracketing experiments¹⁸ were carried out measuring the rate of protonation of CF₃C₆H₅ by BH⁺ and the rate of deprotonation of $[CF_3C_6H_5]H^+$ by B at 300 K. The reactant $[CF_3C_6H_5]H^+$ and BH^+ ions were generated by the methane chemical ionization of CF3C6H5 or B ($P = 10^{-4}$ mbar) in the external ion source, transmitted into the cell, and isolated by broad band ejection and by "single shots". Their thermal equilibration was ensured by multiple collisions with Ar admitted by a pulsed valve up to the pressure of ca. 1×10^{-5} mbar. After 0.5 s pumping time, mass spectra were recorded at increasing reaction time, yielding a temporal

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TABLE 1: Protonation of CF₃C₆H₅ by Gaseous Acids BH⁺

В	PA(B) (kcal/mol) ^a	GB(B) (kcal/mol) ^a	k^b	eff (%) ^c	$C_{6}H_{5}CF_{2}^{+}/[CF_{3}C_{6}H_{5}]H^{+}$
CH_4	131.6	126.0	3.6	~ 100	75:25
SO_2	152.1		2.1	70	70:30
C_2H_4	162.6	155.6	2.8	77	80:20
(CF ₃) ₂ CHOH	165.0	157.2	1.7	~ 100	100:0
H_2O	166.5	159.0	4.0	~ 100	100:0
CF ₃ CH ₂ OH	169.0	161.2	1.7	94	100:0
CF ₃ COCH ₃	174.2	166.4	1.4	79	100:0
CH ₃ NO ₂	179.2	171.7	0.94	29	$100:0^{d}$
$CH_3CH=CH_2$	179.5	171.7	0.38	16	100:0
$(CH_3)_2O$	192.1	184.3	< 0.02	< 0.8	100:0

^{*a*} Reference 18. ^{*b*} × 10⁹ cm³ molecule⁻¹ s⁻¹. ^{*c*} Efficiency: k/k_{coll} . The collisional rate constant, k_{coll} , was calculated according to ref 23. ^{*d*} The C₆H₅CF₂⁺ product ion is in part (ca. 30%) associated to CH₃NO₂.

profile of the relative abundancies of reactant and product ions. The decay of the reactant ion intensity with time was due either to a unimolecular decomposition or to a bimolecular reaction, as verified by the dependence of the time constant on the pressure of the added neutrals. In the case of bimolecular processes, pseudo-first-order rate constants of the ion-molecule reactions were derived from the exponential decrease of the reactant ion abundance vs time and converted to absolute rate constants from the known neutral pressure. The major error in rate constants (estimated to be $\pm 30\%$) arises from uncertainties in absolute pressure determination. The concentration of the neutrals was determined from the pressure reading at the ionization gauge located in the high-vacuum line of the ICR cell housing. The ionization gauge was calibrated with the reference reaction $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$ using the wellestablished rate constant value of 11.7×10^{-10} cm³ molecule⁻¹ s⁻¹.¹⁹ The crude value of the neutral pressure was corrected by the relative ionization cross sections due to different polarizabilities.20

Radiolytic Experiments. The gaseous samples to be submitted to γ -irradiation were prepared in Pyrex vessels (135 mL) according to standard vacuum procedures. Following the introduction of the gaseous components into carefully outgassed bulbs, the latter were sealed and then irradiated in a 60Co 220 Gammacell (Nuclear Canada Ltd) at 40 °C, for 2 h at the dose rate of 5×10^3 Gy h⁻¹. As usual in radiolytic experiments run to elucidate mechanistic and kinetics features of ion-molecule reactions, the conversion of the substrate into products is kept lower than 1%. The radiolytic products were recovered as n-hexane solution after thorough washing of the vessel inner walls by repeated freeze-thaw cycles and were analyzed by GLC and GLC/MS using a Perkin Elmer 8700 gas chromatograph equipped with a flame ionization detector and a Hewlett Packard 5890 A gas chromatograph in line with a HP 5970B mass-selective detector. The column used was a 100 m long, 0.25 mm i.d. silica column coated with a 0.50 μ m film of nonpolar-bonded methylsilicone (Petrocol column from Supelco Co.).

Computational Details. Ab initio quantum-mechanical calculations were performed by using an IBM RISC/6000 version of the Gaussian 94 set of programs.²¹ The geometries of the investigated species were optimized and characterized as true minima by vibrational analysis at the HF/6-31G* level of theory. Their zero-point vibrational energies were obtained by the HF/6-31G* frequencies uniformly scaled by a factor of 0.894. Single-point calculations were performed at the MP2-(full)/6-31G* level of theory, in order to include the correlation energy effects on the relative stabilities of the investigated structures. The 0 K total energies of the species under study were corrected at 298.15 K by adding the rotational (3/2RT), translational (3/2RT) and vibrational contributions at this temperature. The last term was calculated by standard statistical

thermodynamics using the scaled HF/6-31G* vibrational frequencies. The 298.15 K energy differences were corrected to enthalpy differences by assuming ideal gas behavior and adding the proper ΔnRT contribution. The calculated harmonic frequencies and the optimized geometries of the species are available from the authors upon request.

Results and Discussion

FT-ICR Proton Transfer Reactions. Many proton transfer equilibria involving benzene derivatives have been the focus of detailed studies which yielded valuable information on the gas-phase basicity, the proton affinity and in some cases on the protonation site of the neutral molecule of interest.^{8–12,18,22} However a similar equilibrium study on the protonation of $CF_3C_6H_5$ turned out not to be feasible, at least by the ICR technique exploited in this study, due to the incursion of an irreversible dissociative proton transfer reaction (pathway a/b or c in eq 2). The tendency of the system to evolve by the

dissociative pathway is such that $C_6H_5CF_2^+$ is the only ionic product from the protonation of CF₃C₆H₅ by acids weaker than $C_2H_5^+$ (Table 1), a finding which is in line with the reported ease of HF loss from CF3-substituted arenium ions.¹⁶ However, whether CF3-substituted arenium ions are the only active intermediates in HF loss is open to question. The use of a kinetic bracketing technique has revealed that strong acids, such as CH5⁺, SO2H⁺, and C2H5⁺ do indeed yield [CF3C6H5]H⁺ ions, which survive long enough despite their energetic formation mode. In fact, the [CF₃C₆H₅]H⁺ ions so formed undergo a slow unimolecular decay by HF loss, at a rate ($k = 0.08 \text{ s}^{-1}$) unaffected by the presence and pressure $(0.8 - 2.5) \times 10^{-8}$ mbar) of neutrals such as Ar, CF₄, and CF₃C₆H₅ itself. The low rate of thermal dissociation allows one to study the faster bimolecular decay following selection of [CF₃C₆H₅]H⁺ ions in the presence of reactive bases (B). As shown in Table 2, the reaction efficiencies increase consistently with increasing PA of B. At the same time the product composition changes from $C_6H_5CF_2^+$ as major product (90% with B = (CF_3)_2CHOH or D_2O) to BH⁺ as major ion formed from the reaction with strong bases. The weakest bases used thus appear to "catalyze" the decomposition of $[CF_3C_6H_5]H^+$ into $C_6H_5CF_2^+$ and HF. These bases conceivably allow the conversion of a relatively inert [CF₃C₆H₅]H⁺ isomeric ion population into [CF₃C₆H₅]H⁺ isomers active toward HF loss. This is bound to occur within the $\{[CF_3C_6H_5]H^+ \cdot B\}$ collision complex.

The general reactivity pattern is consistent with the existence of two distinct $[CF_3C_6H_5]H^+$ isomers or mixture of isomers,

TABLE 2: Deprotonation of $[CF_3C_6H_5]H^+$ by Reference Bases (B)

В	PA (kcal mol ^{-1}) ^{a}	k^b	eff (%) ^c	BH ⁺ /C ₆ H ₅ CF ₂ ⁺ product ions
(CF ₃) ₂ CHOH	165.0	0.17	1.8	10:90
D_2O	166.5	0.44	3	10:90
CF ₃ CO ₂ H	169.0	0.40	16	50:50
$CH_2(CN)_2$	175.6	1.1	22	40:60
CH ₃ NO ₂	179.2	0.93	28	60:40
C_6D_6	181.3	0.32	32	100:0
$(CH_3)_2O$	192.1	0.5	40	90:10
(EtO) ₂ CO	>202.7	1.1	100	100:0

^{*a*} Reference 18. ^{*b*} ×10⁹ cm³ molecule⁻¹ s⁻¹. The exponential decays of the relative intensity of reactant ions at m/z 147 were corrected by the contribution due to unimolecular loss of HF. ^{*c*} See note *c* of Table 1.

characterized by a markedly different ease to undergo HF loss. The first one, resistant to HF loss, is likely to correspond to a ring-protonated species, most probably a m- or p-protonated isomer or a mixture of the two with a possible contribution of ipso- or o-protonated forms. Such an ion population, henceforth designated as $CF_3C_6H_6^+$, besides displaying a kinetic barrier to decomposition, also shows threshold energy requirements to its formation, which is achieved by proton transfer from $C_2H_5^+$ but not obtained from $(CF_3)_2CHOH_2^+$ (Table 1). In the absence of a significant kinetic barrier to proton transfer involving unhindered arenium ions,²⁴ it appears that the PA of CF₃C₆H₅ at the m/p-sites may be as low as 165.0 kcal mol⁻¹. At the other extreme, the weakest BH+ acids yielding exclusively C6H5- CF_2^+ are suggested to do so by the intermediacy of a F-protonated species, an ion population henceforth designated as C₆H₅CF₂FH⁺. The F-protonated isomer is in fact expected to have the features of a [C₆H₅CF₂⁺•FH] ion-dipole complex.^{5,25} The loss of HF, whereas unfavorable on enthalpy grounds by the HF binding energy, is associated with an entropic gain. The balance of the two factors clearly emerges from the fact that the inefficient reactions of the weakest BH⁺ acids yield exclusively C₆H₅CF₂⁺, with no trace of C₆H₅CF₂FH⁺ being formed. This finding suggests that, upon protonation of CF₃C₆H₅ by weak BH⁺ acids, the systems evolves toward a ternary product complex, [C₆H₅CF₂⁺•FH•B], which undergoes prompt dissociation. The entropic gain of the latter process apparently outweighs the binding enthalpy of HF or B with C₆H₅CF₂⁺. This finding also confirms that the bracketing criterion is governed by the standard free energy change rather than by reaction enthalpy.²⁶ It is worth noting that when B is a base endowed with strong binding properties to positive ions²⁷ (B = CH₃NO₂), the dissociation is limited in part to [C₆H₅- $CF_2^+ \cdot B] + HF.$

The same body of evidence disproves any possible involvement of ipso- or o-protonated forms in the reaction of $CF_3C_6H_5$ with weak acids. In fact, the limited amount of excess energy delivered by the mild protonation process would place a ringprotonated species at an energy level comparable to that experienced by the genuine ipso-complex formed by the CF_3^+ attack to benzene in the high-pressure radiolytic experiments. In such a case, we should expect a similarly high fraction of $CF_3C_6H_6^+$ ions surviving dissociation. It should also be noted that HF loss from ground state ipso- or o-protonated species formally involves 1,2- and 1,3-elimination processes, hardly compatible with the exceedingly fast fragmentation process observed.⁵

The efficiency of dissociative proton transfer from BH⁺ to CF₃C₆H₅ shows a marked decrease in correspondence to B = CH₃NO₂, CH₃CHCH₂. These two bases should therefore verify the condition of ergoneutral reaction ($\Delta G^{\circ} = 0$). The free



Figure 1. Qualitative free energy profile as deduced from ICR bracketing experiments.



Figure 2. HF/6-31G* optimized geometry of F-protonated CF₃C₆H₅.

energy change for the dissociative proton transfer H^+ + $CF_3C_6H_5 \rightarrow C_6H_5CF_2^+$ + HF should therefore be approximately equal to $-171.7 \text{ kcal/mol}^{-1}$, being the gas-phase basicity (GB) of both CH₃NO₂ and CH₃CHCH₂ equal to $171.7 \text{ kcal mol}^{-1}$ (see Table 1).¹⁸

Ab Initio MO Calculations. As long as the overall reaction pattern observed in ICR experiments is dominated by the irreversible, entropically favored loss of HF from C₆H₅CF₂FH⁺, little information can be gained on the relative stabilities of isomeric [CF₃C₆H₅]H⁺ species. The absence of D incorporation into C₆H₅CF₂⁺ ions from the reaction of D₂O or C₆D₆ with CF₃C₆H₆⁺ suggests that a fast [B·CF₃C₆H₆⁺] \Rightarrow [BH⁺·CF₃C₆H₅] \rightarrow [B·C₆H₅CF₂FH⁺] \rightarrow B + HF + C₆H₅CF₂⁺ dissociation process. This may, however, reflect relative free energies rather than enthalpic factors. The likely free energy profile of the proton transfer reactions involving CF₃C₆H₅ is shown in Figure 1.

To gain information on the energetics of the conceivable [CF₃C₆H₅]H⁺ isomers, MP2/6-31G* ab initio MO energy calculations were performed on HF/6-31G* optimized geometries, yielding the data collected in Table 3. The relative stabilities of isomeric ions and the derived proton affinities of specific sites of CF₃C₆H₅ show that F protonation is favored over ring protonation, though not by a large extent. The geometry of the F-protonated isomer (Figure 2) shows two distinct moieties, an almost unperturbed α, α -difluorobenzyl cation associated with a HF molecule pointing the F atom toward the benzyl carbon (CCF angle = 108.2° ; CFH angle = 160.3°). As compared to the C-F bond in α, α, α -trifluorotoluene (1.32) Å), the C-F distance is elongated to 2.62 Å (HF/ $6-31G^*$). This geometry suggests that the F-protonated isomer can be envisioned as an ion–dipole complex between α, α -difluorobenzyl cation and neutral HF, in agreement with the negligible positive charge on HF (ca. 0.022 according to Mulliken population analysis). Also, the relative stability of C₆H₅CF₂FH⁺ with respect to C₆H₅CF₂⁺ and HF, corresponding to a binding enthalpy of 10.3 kcal mol⁻¹ ($\Delta E_{\text{binding}} + RT$), is in the range expected for an ion-dipole complex. The dissociation of HF results to be energetically unfavorable from all [CF₃C₆H₅]H⁺

TABLE 3: Calculated SCF and MP2 Total Energies (*E*, hartrees molecule⁻¹), Relative Stabilities (ΔE , kcal mol⁻¹), and Site-Specific Proton Affinities (PA, kcal mol⁻¹)

				MP2 (full)/6-31G*//HF/6-31G*		
species	E(HF/6-31G*)	<i>E</i> (MP2(full)/6-31G*//HF/6-31G*)	ZPE (HF/6-31G*)	$\Delta E (0 \text{ K})$	Δ <i>E</i> (298 K)	PA
CF ₃	-566.32554	-567.75397	0.10170	170.3	168.8	
CF ₃ H+	-566.61316	-568.03259	0.10882	0	0	170.3
H CF ₃	-566.61746	-568.02670	0.11225	5.8	4.5	165.8
CF ₃ H H	-566.61946	-568.02930	0.11162	3.8	2.6	167.7
CF ₃ (+) H H	-566.62120	-568.02842	0.11140	4.2	3.0	167.3
CF ₃	-566.60005	-568.02351	0.11128	7.2	6.1	164.2
+CF ₂	-466.59558	-467.83112	0.0986	10.4	9.7	
HF	-100.00291	-100.18358	0.00888			

isomers, in contrast with recent semiempirical calculations predicting $C_6H_5CF_2^+ + HF$ to be ca. 20 kcal mol⁻¹ more stable than ipso-protonated $CF_3C_6H_5$.^{16b} The ab initio calculations thus confirm that the dissociative proton transfer process is entropically driven.

Proton Transfer Reactions from Radiolytically Formed CF₃C₆H₆⁺ Ions. The finding of an appreciable efficiency for the deprotonation reaction of CF₃C₆H₆⁺ ions by benzene (efficiency = 32%) under ICR conditions prompted us to use the trifluoromethylation reaction by radiolytically formed CF₃⁺ as a convenient way to point out and study the proton transfer between truly ground state arenium ions and benzene. The trifluoromethylation of benzene by CF₃⁺ ions under radiolytic conditions is a well-characterized ionic process,^{15a,n} where the ionic reactant and intermediates may attain thermal equilibration by unreactive collisions with the bulk gas before undergoing reaction.

Within the general outline of gas-phase electrophilic aromatic substitution, the highly exothermic addition of CF_3^+ to benzene^{15a} involves intermediacy of a σ -complex (eq 1), which in the medium will undergo fast 1,2-H/D shifts and collisional quenching yielding ultimately the ground state most stable species. Based on the reported ab initio MO calculations, the latter ones are likely to be the o- or m-protonated species or a mixture of the two, collectively indicated as **I** in eq 3. Intermediate **I** arises from CF_3^+ attack to C_6H_6 (a symmetrical scheme can be drawn for primary attack to C_6D_6) and can be competitively deprotonated by C_6H_6 , C_6D_6 and $(EtO)_2CO$ with rate constants k_{ben} (assumed equal for C_6H_6 and C_6D_6) and k_{base} , respectively.

At increasing relative concentrations of a strong base $((C_2H_5O)_2CO)$, able to intercept ionic intermediates with unit efficiency, deprotonation of I by the base will increasingly



compete with proton transfer process to C_6D_6 yielding **II** and hence larger amounts of $CF_3C_6H_5$ will be formed with respect to C_6D_5H . Figure 3 shows product yield ratios from the mirror reactions of $CF_3^+ + C_6H_6$ and $CF_3^+ + C_6D_6$ occurring within the same gaseous system. The two product ratios, $[CF_3C_6H_5]/[C_6D_5H]$ and $[CF_3C_6D_5]/[C_6DH_5]$, obviously display an analogous dependence on the experimental conditions. These ratios are predicted to follow a linear dependence on the base/benzene concentration ratio, when the conventional steady state treatment is applied to intermediates **I** and **II** and when the $[C_6H_6]/[C_6D_6]$ ratio is held constant. Equation 4 is derived for the product

$$\frac{[CF_3C_6H_5]}{[C_6D_5H]} = 7/6 \left\{ \frac{k_{\text{base}}[B]}{k_{\text{ben}}[C_6D_6]} + \frac{[C_6H_6]}{[C_6D_6]} + 1 \right\}$$
(4)

ratio from the reaction of CF_3^+ with C_6H_6 (eq 3) in the hypothesis of complete H/D randomization within **II** and neglecting any H/D kinetic isotope effect arising from deprotonation of **II** by B. Obviously, a similar equation holds for the CF_3^+/C_6D_6 reaction. The linear plots shown in Figure 3 verify the kinetic scheme adopted. The hypothesis of fast H/D



Figure 3. Plots of $[CF_3C_6X_5]/[C_6XY_5]$ vs $[B]/[C_6Y_6]$ concentration ratio from the radiolytic reaction of CF_3^+ with the C_6H_6/C_6D_6 mixtures (\blacktriangle , X = H, Y = D; \triangle , X = D, Y = H). The composition of the gaseous systems (Torr) was as follows: C_6H_6 ([¹²C6]benzene (99.9 at % ¹²C): 3.6-4.1); C_6D_6 (benzene- d_6 (99.95 atom % D): 3.7-4.3); B ((EtO)₂CO: 0.17-4.4); CF₄ (650); NO (20).

shift within **II** is verified by the linearity of the plot and by the value of the intercept which would otherwise exceed the term $7/6\{([C_6H_6]/[C_6D_6]) + 1\}$. Relatively fast H/D shifts within II conceivably result from the exothermicity of the proton transfer process from $CF_3C_6{H_6}^+$ ions to benzene (${\geq}13$ kcal mol⁻¹)¹⁸ since thermoneutral 1,2-H/D shifts within thermalized arenium ions were found to occur in the $10^{-7}-10^{-8}$ s time scale.²⁸ The slopes of the linear plots, equal to $k_{\text{base}}/k_{\text{ben}}$, allow us to estimate the rate of deprotonation of ions I by $(C_2H_5O)_2$ -CO relative to benzene. Their relative magnitude, $k_{\text{base}}/k_{\text{ben}} =$ 3.0 ± 0.4 , obtained under radiolytic conditions, is remarkably close to that obtained from ICR data of Table 2, wherein (C₂H₅O)₂CO deprotonates CF₃C₆H₆⁺ at the collision rate and ca. 3 times faster than C_6H_6 . This finding appears noteworthy if one considers the very different pressure regimes of the two techniques under comparison and supports the idea that deprotonation of arenium ions by a strong base occurs at a collision rate, which can be estimated by parametrized ADO calculations.²³ This confirms an assumption previously held in a number of cases.²⁸ The derived value of $k_{\text{ben}} = (3 \pm 0.4) \times$ 10^{-10} cm³ molecule⁻¹ s⁻¹ for the proton transfer between radiolytically generated ions I and benzene represents the direct estimate of the rate of intermolecular proton transfer involving aromatic transient ions in thermal equilibrium with the gaseous environment. However, it should not be taken for granted that the high-pressure radiolytic medium does ensure fast thermal equilibration of reactive intermediates. For instance, this condition is not met in the trifluoromethylated arenium ions from CF₃⁺ attack to C₆D₅CH₂CH₂C₆H₅ undergoing fast multiple H^+/D^+ transfer between the trifluoromethylated and the spectator ring.^{15d} In this system the proximity of the second phenyl ring promotes H^+/D^+ transfer from the CF₃-substituted arenium ring before the latter had a chance to dissipate its excess energy by unreactive collisions, initiating an extensive sequence of interannular H/D exchange.

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