Lifetimes of Gaseous Ion – Neutral Complexes:
The Rate of Isotopic Scrambling within Ethyl Ions as an Internal Clock

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Abstract: The lifetimes of typical ion – neutral complexes (INCs), the charged intermediates of electrophilic aromatic alkylation, were investigated by a kinetic approach that utilizes as an internal clock the rate of H/D scrambling within labeled carbenium ions bound to a nucleophile as an INC. The specific process investigated was the aromatic ethylation promoted by addition of a $CF_3C_6X_6^+$ (X = D or H) arenium ion to ethylene, C_2Y_4 (Y = H or D). This process belongs to a class of reactions, the so-called Crafts – Friedel alkylation, that was previously demonstrated to occur within gaseous INCs and represents an alternative to electrophilic aromatic substitution. Following preliminary study by Fourier-transform ion cyclotron resonance (FT-ICR) and triple-quadru-pole (TQ) mass spectrometry, the reaction was investigated by the radiolytic technique in CF_4 at 720 Torr in the temperature range from 298 to 393 K, by measuring the D(H) incorporation into the α position of the side chain of the ethylated products $CF_3C_6X_4C_2Y_4X$. Kinetic analysis of the results led to lifetimes of 2.0×10^{-10} s (298 K), 1.2×10^{-10} s (315 K), 4.4×10^{-11} s (353 K) and 1.9×10^{-11} s (393 K) based on the H/D scrambling within $C_2H_4D^+$, whereas the lifetime deduced from H/D scrambling within $C_2D_4H^+$ is 9.0×10^{-12} s at 393 K. The results are discussed and compared with those of an independent approach based on a chemical activation technique.

Keywords: automerizations · Crafts – Friedel reactions · ion – neutral complexes · ion – molecule reactions · kinetics

Introduction

The interest in gaseous ion – neutral complexes (INCs) is currently increasing due to the growing recognition of their value as simplified and generalized models in many areas of ionic chemistry, in addition to their long-established role in bimolecular ion – molecule reactions and in the unimolecular fragmentation of excited ions.[1–16]

The wide interest and applications of the concept of INCs has stimulated the study of their properties, in particular of their lifetime, by a variety of theoretical and experimental techniques, including trajectory calculations, fast photoelectron spectroscopy (FPS), flowing afterglow (FA), selected-ion flow tube (SIFT), ion mobility spectroscopy (IMS), resonant two-photon ionization mass spectrometry (R2PIMS), and high-pressure mass spectrometry (HPMS).[17–25] Despite such
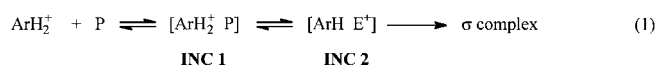
sustained interest the data currently available on the most interesting INCs, those which undergo intracluster reactions, are few in number and subject to unusually large uncertainties, a situation that justifies the search for new approaches.

In a preceding paper we reported a high-pressure chemical activation study[26] which allowed us to estimate the lifetime of INCs that are key intermediates in a recently discovered, typically intracluster reaction that represents an alternative to conventional aromatic alkylation.[27–30]

Here we report a different approach to the evaluation of the lifetime of INCs involved in the same reaction, where the extent of H/D scrambling within a $C_2H_4D^+$ or $C_2D_4H^+$ ethyl ion, confined together with an aromatic molecule within the gaseous complex, is utilized as an internal clock.

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Methodology

We utilized one of the so-called Crafts – Friedel reactions, an alternative to conventional alkylation which is known to occur within gaseous INCs according to the Equation (1), where ArH_2^+ denotes an arenium ion and P a proelectrophile, that is

$$ArH_2^+ + P \rightleftharpoons [ArH_2^+ P] \rightleftharpoons [ArH\ E^+] \longrightarrow \sigma\ complex \qquad (1)$$

$$\qquad\qquad\qquad \textbf{INC 1} \qquad\qquad \textbf{INC 2}$$

a species capable of producing the electrophile E^+ upon protonation.

In principle, the lifetime of **INC2**, which is the time interval between its formation from **INC1** and its conversion into the σ complex, can be evaluated if E^+, before alkylating the arene, undergoes some structural change whose extent can be deduced from the composition of the products. Several conditions must be met in order to implement the above strategy: firstly, the rate of change of E^+ should be known with reasonable accuracy and be commensurate to the lifetime of **INC2**. Secondly, since the rate of change of E^+ depends on temperature, the conversion **INC1** → **INC2** should be nearly thermoneutral, allowing one to consider the temperature of **INC2** to be equal to that of **INC1**, and hence to the experimentally measurable temperature of the bath gas.

The above considerations suggested the choice of $CF_3C_6X_5$ (X = D or H) and C_2Y_4 (Y = H or D) as a suitable reagent pair since, in this case, the proton affinity (PA) of the arene *exceeds* that of the olefin (vide infra), ensuring that **INC2** formed upon intracomplex H^+ (D^+) transfer from **INC1** does not contain excess internal energy. Moreover, the ethyl cation, which is reagent E^+ in **INC2**, is known to undergo the low-barrier process shown in Equation (2).

$$Y_2C \overset{X}{\underset{\mathbf{1a}}{\cdots\overset{+}{\cdots}}} CY_2 \longrightarrow \underset{\mathbf{2(TS)}}{XY_2C\!-\!CY_2^+} \longrightarrow XYC \overset{Y}{\underset{\mathbf{1b}}{\cdots\overset{+}{\cdots}}} CY_2 \quad (2)$$

According to extensive theoretical and experimental studies,[31–41] the nonclassical ion **1** is the most stable structure, the classical ion **2** being identified as the transition state for process (2). Reasonably accurate computation of the height of the barrier for this reaction is well within the capabilities of modern ab initio methods, allowing the rate constant for

process (2) to be evaluated within the framework of current theories of unimolecular reaction kinetics. The occurrence of isotope-scrambling reaction (2) affects the composition of the products, in that alkylation of the arene by **1a** is expected to yield products containing X only in the β position of the side chain, whereas the product from **1b** should contain X in both the α and the β positions. It follows that the experimental determination of the distribution of Y in the side chain of the products allows one, in principle, to evaluate the extent of reaction (2) and hence, utilizing its theoretically computed rate constant, the lifetime of the ethyl ion within **INC2**, which corresponds to the lifetime of the complex. The specific experimental requirements suggested recourse to the radiolytic technique, characterized by two features essential to this study, namely the high operating pressure required to ensure efficient thermalization of the INC, and the positive characterization of the products, especially with respect to their isomeric and isotopic composition.[42] Supporting evidence was obtained from Fourier transform ion cyclotron resonance (FT-ICR) and triple quadrupole (TQ) mass spectrometry.

Experimental Section

Materials: The gases were research-grade products from Matheson Gas Products or Aldrich Chemical Company with a stated purity of 99.95 mol % (O_2, CF_4, SF_6, C_2H_4), with the exception of C_2D_4, which was obtained from Cambridge Isotope Laboratories and had a stated isotopic purity of greater than 99 atom %. All chemicals used in the radiolysis or as mass-spectrometric standards were prepared and purified according to established procedures utilizing research-grade products from commercial sources. C_6D_6 with a stated isotopic purity of 99.96 atom % was obtained from Aldrich.

Instruments: The FT-ICR mass spectra were recorded with a Bruker Spectrospin APEX TM 47e spectrometer equipped with an external ion source, a cylindrical infinity cell, and an X Mass data system. The triple-quadrupole instrument was a VG Micromass model Quattro spectrometer in which the $C_6D_6CF_3^+$ ions, generated in the ion source by CF_4/C_6D_6 CI (10^{-4} Torr) and selected with the first quadrupole (Q1), were driven (nominal center-of-mass kinetic energy from 0.15 to 1.0 eV) into the RF-only hexapolar cell containing C_2H_4 at nominal pressures up to 10^{-4} Torr; the products were analyzed in the third quadrupole (Q3) at a scan frequency of 150 amu s^{-1}. The radiolytic products were analyzed with a Hewlett–Packard 5890 GC equipped with an FI detector and a VG Micromass TRIO benchtop GC/MS, utilizing a 50-m long, 0.2-mm i.d. fused-silica capillary column, coated with a 0.5-μm layer of cross-linked methylsilicone phase (PONA column from Hewlett–Packard), operating in the temperature range from 70 to 180 °C.

Radiolytic experiments: The gaseous samples were prepared by standard techniques in a greaseless vacuum line in sealed 135 mL Pyrex ampoules. The irradiations were performed in a 220 Gammacell (Nuclear Canada Ltd.) equipped with a thermostatic device designed to maintain the sample temperature within ±1 °C in the range from 298 to 393 K.

In addition to the bulk gas (CF_4 or CH_4) at a pressure of 720 Torr, all systems contained a radical scavenger (O_2, 10 Torr), a thermal-electron scavenger (SF_6, 5 Torr), and a base (Et_3N, 0.2 Torr). The irradiation time was 2 h to a total dose of about 10^4 Gy. After the irradiation, the vessels were cooled to 77 K, outgassed and allowed to warm up following addition of methanol. After careful rinsing of the inner walls of the vessels, the solution obtained was utilized for the analysis of the products. The D content in the α and β positions of the side chain of o-, m-, and p-$CF_3C_6D_4C_2H_4D$ was measured by GC/MS, by comparing the intensity of the molecular ion with that of the fragment formed by loss of the methyl group (CH_3 or CH_2D); corrections were applied for the ^{13}C contribution and the incomplete labeling of C_6D_6. The occurrence of H(D) scrambling within the alkyl chain and between the alkyl chain and the ring in the

Abstract in Italian: *Un metodo cinetico nel quale la velocità del mescolamento isotopico H/D in ioni carbenio funge da orologio interno è stato applicato alla valutazione della vita media di tipici complessi ione-molecola in fase gassosa. Si è utilizzata l'etilazione promossa dall'addizione di ioni arenio $CF_3C_6X_5^+$ (X = H, D) a C_2Y_4 (Y = D, H), una reazione cosiddetta di 'Crafts–Friedel' che comporta la formazione di complessi ione-arenio/olefine, la loro conversione in complessi arene/ione carbenio e la conversione di questi ultimi in addotti σ. La reazione investigata preliminarmente mediante spettrometria di massa (FT-ICR, triplo quadrupolo) è stata studiata con la tecnica radiolitica in CF_4 a 720 Torr a temperature da 293 a 393 K, misurando l'incorporazione di D(H) nella posizione α della catena laterale degli etil(trifluorometil)benzeni formati. L'analisi cinetica ha portato a vite medie del complesso ione/molecola di $2,0 \times 10^{-10}$ s (298 K), $1,2 \times 10^{-10}$ s (315 K), $4,4 \times 10^{-11}$ s (353 K) e $1,9 \times 10^{-11}$ s (393 K), basate sulla velocità di mescolamento H/D nello ione $C_2H_4D^+$. L'unica misura basata sulla velocità di mescolamento nello ione $C_2D_4H^+$ è stata effettuata a 393 K e fornisce una vita media di $9,0 \times 10^{-12}$ s. I risultati sono discussi e paragonati con quelli in precedenza ottenuti con un tecnica di attivazione chimica.*

molecular ion obtained by 70 eV EI was excluded by control experiments with authentic samples of the CF_3–C_6H_4–CH_2CD_3 and CF_3–C_6D_4–C_2H_5 isomers. The same analytical procedure was employed for the determination of H-content in the α and β positions of the side chain of the $CF_3C_6H_4C_2D_4H$ isomers. The results were corrected in this case for the incomplete labeling of C_2D_4.

Computational details: The theoretical studies of the $C_2H_5^+$ ions cited above demonstrate the existence of two structures, the bridged (nonclassical) ion **1** and the classical ion **2**, whose calculated relative stabilities depended on the level of theory employed.[35–41] Ab initio calculations at the MP4SDTQ/6-311 G (d,p)//MP2/6-31G (d) level of theory identified **1** (C_{2v} symmetry) as the global minimum, whereas **2** (C_s symmetry) is the transition state for H scrambling, and is less stable by 7 kcal mol^{-1}. However, such a small difference in stability called for a higher level theoretical treatment. To this end, ab initio calculations at the G2 level of theory[43] were performed by employing an IBM RISC/6000 version of Gaussian 94.[44] The $C_2H_4D^+$ and $C_2D_4H^+$ total energies were calculated at 0 K and corrected to the temperatures of 298, 315, 353, and 393 K by adding translational, rotational, and vibrational contributions, calculated by standard statistical equations,[45] and treating the system as a canonical ensemble. The absolute entropies of **1** and **2** were computed according to standard statistical-mechanics procedures by employing the scaled HF/6-31G (d) harmonic frequencies and the moments of inertia calculated from the optimized geometries.

Results and Discussion

Mass spectrometric experiments: A preliminary investigation of reaction sequence (1) was performed with experimental techniques, such as FT-ICR and TQ mass spectrometry, capable of establishing parent–daughter relationships in ion–molecule reaction sequences. The FT-ICR experiments involved formation of $CF_3C_6D_6^+$ ions in the external source, their introduction into the resonance cell, collisional cooling by argon admitted for a short period through a pulsed valve, isolation by selective-ejection techniques, and reaction with C_2H_4, present at stationary pressures from 10^{-8} to 10^{-7} Torr in the cell. Under these conditions, characterized by very inefficient collisional stabilization of excited adducts such as

INC1, no reactions were observed except a slow loss of DF from $CF_3C_6D_6^+$. Significantly, no $C_2H_4D^+$ ions were detected. Analogous experiments were performed by utilizing a TQ mass spectrometer, where $CF_3C_6D_6^+$ ions, formed in the source and mass-selected with the first quadrupole, were allowed to react with C_2H_4 at a pressure of about 10^{-4} Torr in the hexapolar (RF-only) cell. Under such conditions, a readily detectable peak at $m/z = 181$ was observed, suggestive of formation of some $[CF_3C_6D_5C_2H_4D]^+$, again without detectable formation of $C_2H_4D^+$ ions. The evidence from the preliminary mass spectrometric experiments, albeit qualitative, is mechanistically informative. The lack of reactivity of $CF_3C_6D_6^+$ toward C_2H_4 and the failure to detect $C_2H_4D^+$ ions from the FT-ICR experiments suggest that in the low-pressure range back-dissociation of **INC1** is faster than its conversion into **INC2** through intracomplex D^+ transfer. Formation of ions of m/z 181, but not of $C_2H_4D^+$ ions, in the TQ experiments can be interpreted either by assuming that collisionally stabilized **INC1** does not evolve into **INC2**, or, more likely, that it is rapidly converted into **INC2** and into the σ complex, without dissociating to form $C_2H_4D^+$.

Radiolytic experiments: Ionization of gaseous systems containing CF_4 as the bulk component, in the presence of C_6X_6 (X = D or H) and C_2Y_4 (Y = H or D), promotes intracomplex alkylation, according to Scheme 1. Note that this scheme neglects the conceivable reversion of the σ complex to **INC2**, which appears most unlikely. In fact, proto-de-ethylation does not occur to any significant extent in the pressure range typical of the radiolytic experiments, as opposed to proto-de-*tert*-butylation,[46] for instance, and the proton (deuteron) initially bound to the *ipso* carbon of the arenium ion is expected to migrate to other ring positions, by a low-barrier, fast intramolecular shift.[42] The major product is $CF_3C_6X_5$, accompanied by smaller, but readily detectable amounts of $CF_3C_6X_4C_2XY_4$ isomers (Table 1). The unusual orientation,

Scheme 1.
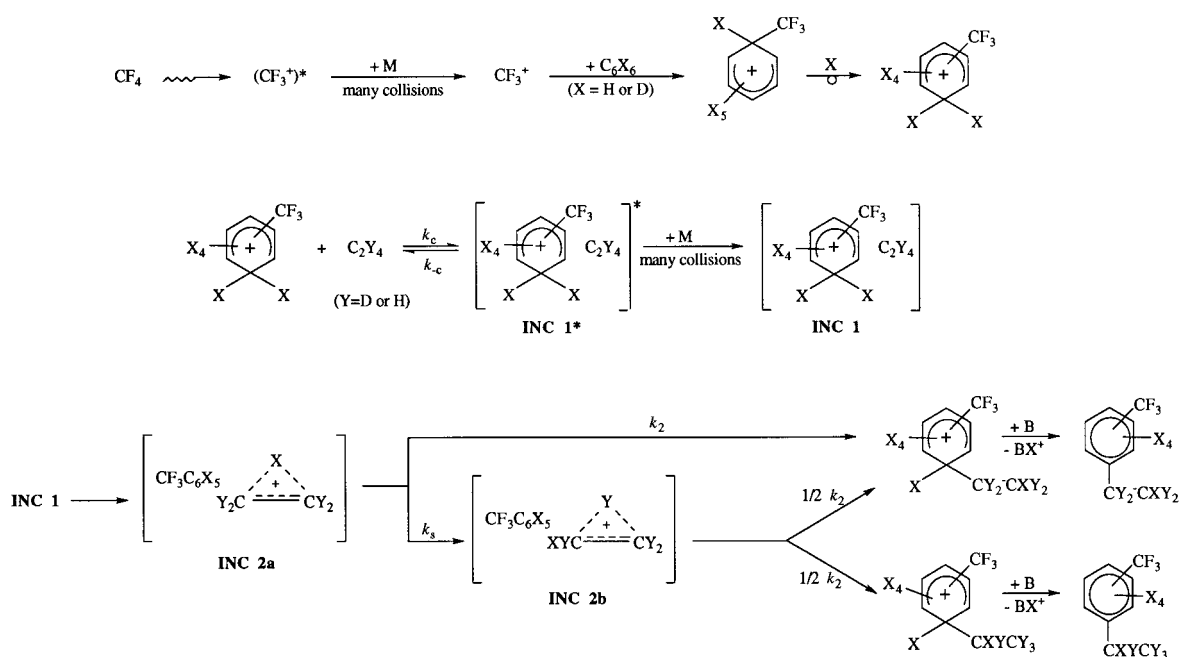
Table 1. Gas-phase radiolytic ethylation of trifluoromethylbenzene.[a]

T(K)	Reagents (Torr)	$[CF_3C_6X_4C_2XY_4]/$ $[CF_3C_6X_5]$	Orientation $(o:m:p)$	Extent of isotopic scrambling (%)[b]			
				ortho	*meta*	*para*	average
intracomplex ethylation of $CF_3C_6D_5$ by $C_2H_4D^+$ in CF_4 (720 Torr)							
298	$C_6D_6(10)$, $C_2H_4(18)$	0.03 ± 0.01[c]	44:46:10	5.0 ± 0.8	9.0 ± 0.5	9.0 ± 1.0	7.2 ± 1.1
315	$C_6D_6(10)$, $C_2H_4(18)$	0.04 ± 0.02[c]	44:46:10	5.5 ± 0.8	9.8 ± 0.4	9.6 ± 0.7	7.9 ± 1.1
353	$C_6D_6(10)$, $C_2H_4(18)$	0.03 ± 0.01[c]	44:46:10	6.0 ± 1.0	11.1 ± 1.0	10.0 ± 1.0	8.5 ± 1.4
393	$C_6D_6(10)$, $C_2H_4(18)$	0.03 ± 0.01[c]	46:46:8	6.2 ± 0.5	12.0 ± 0.5	14.4 ± 0.7	9.4 ± 1.0
intracomplex ethylation of $CF_3C_6H_5$ by $C_2D_4H^+$ in CF_4 (720 Torr)							
315	$C_6H_6(10)$, $C_2D_4(35)$	0.18 ± 0.04[d]	51:45:4	[e]	[e]	[e]	[e]
393	$C_6H_6(10)$, $C_2D_4(25)$	0.07 ± 0.01[d]	50:45:5	$1.3 - 0.1$	2.4 ± 0.1	2.6 ± 0.7	2.0 ± 0.2
conventional ethylation of $CF_3C_6H_5$ by $C_2H_5^+$ in CH_4 (720 Torr)							
315	$CF_3C_6H_5(5)$	–	46:45:9				

[a] All systems contained a base (Et$_3$N, 0.2), a radical scavenger (O$_2$, 10 Torr), and a thermal-electron scavenger (SF$_6$, 5 Torr). [b] Fraction of the $CF_3C_6X_4C_2XY_4$ molecule containing the X atom in the α position of the side chain. [c] X = D, Y = H. [d] X = H, Y = D. [e] Below detection limit.

characterized by predominantly *ortho/meta* substitution, is not peculiar to intracomplex alkylation. Rather, the same isomeric composition characterizes the products from the direct, conventional ethylation promoted by $C_2H_5^+$, a major ion from the irradiation of CH_4,[42] according to Equation (3).

$$C_2H_5^+ + CF_3C_6H_5 \longrightarrow [CF_3C_6H_5C_2H_5]^+ \xrightarrow{+B, -BH^+} CF_3C_6H_4C_2H_5 \quad (3)$$
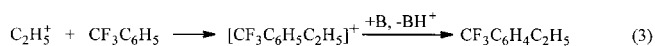
Independent evidence for the higher nucleophilicity of the *ortho* and the *meta* positions of $CF_3C_6H_5$ is provided by a recent study of its local PA.[47] The lack of thermochemical data for ethyltrifluoromethylbenzenes prevents accurate evaluation of ΔH_3^o. However, from the heat of formation of m-$CF_3C_6H_4C_2H_5$ derived by the group additivity approach, taking the PA of the ring position bearing the C_2H_5 group equal to that of the *meta* positions of $CF_3C_6H_5$,[47] and utilizing available thermochemical data,[48] one can roughly estimate that ethylation (3) of the *meta* position of $CF_3C_6H_5$ is exothermic by about 30 kcal mol^{-1}.

The efficiency of intracomplex ethylation is measured by the product ratio $[CF_3C_6X_4C_2XY_4]/[CF_3C_6X_5]$, which is reported in the third column of Table 1 and increases, as expected, with increasing C_2Y_4 concentration. The $CF_3C_6X_6^+$ arenium ions, formed by attack of CF_3^+ on C_6X_6, can undergo two competing processes, namely deprotonation (dedeuteronation) by a gaseous base, B, yielding $CF_3C_6X_5$, or addition to C_2Y_4, resulting in intracomplex ethylation, as depicted in Equations (4) and (5). Here B denotes any component of the gaseous system, including C_6X_6, whose basicity exceeds that of $CF_3C_6X_5$, k_b is a composite rate constant for the deprotonation (dedeuteronation) by the various gaseous bases (C_6X_6, Et$_3$N, etc.) and k_R is a phenomenological, overall rate constant for the intracomplex alkylation.

$$CF_3C_6X_6^+ \begin{array}{c} \xrightarrow{k_b[B]} CF_3C_6X_5 \quad (4) \\ \xrightarrow{k_R[C_2Y_4]} \dashrightarrow CF_3C_6X_4C_2XY_4 \quad (5) \end{array}$$
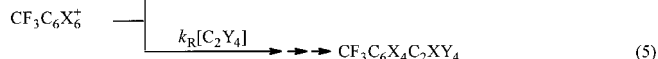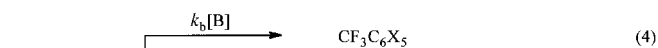
The product ratio from the competitive processes (4) and (5) is given by Equation (6), which accounts for the increase of

$$[CF_3C_6X_4C_2XY_4]/[CF_3C_6X_5] = k_R[C_2Y_4]/k_b[B] \quad (6)$$

the ethylation efficiency at higher $[C_2Y_4]/[B]$, and hence $[C_2Y_4]/[C_6X_6]$, ratios.

As shown in Table 1, the product ratio $[CF_3C_6X_4C_2XY_4]/[CF_3C_6X_5]$ is independent of temperature in the range 298 – 393 K. Since the rate of process (4), proton (deuteron) transfer to gaseous bases of considerably higher PA, is expected to show only a weak temperature dependence,[49] the constancy of the ethylation efficiency over the wide temperature range investigated requires that the rate-determining step of sequence (5) also be nearly temperature-independent. The mass spectrometric evidence examined in the preceding section points to the conversion **INC1→INC2** as rate-determining in the case of interest, consistent with the higher PA of $CF_3C_6H_5$ than of C_2H_4, 167.7 vs 162.6 kcal mol^{-1}.[47, 50] Such a ΔPA would make the proton (deuteron) transfer required for **INC1→INC2** conversion endothermic by some 5 kcal mol^{-1}, ignoring differential solvation effects in the two complexes. If the conversion **INC1→INC2** is indeed rate-determining in Equation (5), its temperature independence suggests that the barriers for the two competing processes undergone by **INC1**, namely back-dissociation and conversion into **INC2**, are nearly equal in CF_4 at 720 Torr.

Isotopic scrambling in ethyl ions: As discussed above, the extent of the H/D scrambling reaction (2) undergone by $C_2XY_4^+$ ions within **INC2** can be deduced from the fraction of the isotope X found in the α position of the side chain of the products, reported in the last four columns of Table 1. In the case of $C_2H_4D^+$, some scrambling is observed, which increases slightly with temperature, as illustrated for the *m*-substituted isomer in Figure 1. Such a limited temperature effect suggests that the activation barriers for the competing processes, that is isotope scrambling within $C_2XY_4^+$ and aromatic ethylation within
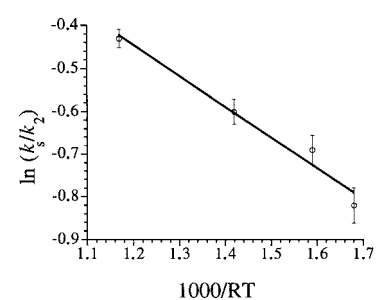

Figure 1. Temperature dependence of the k_s/k_2 ratio for intracomplex *meta*-substitution of $CF_3C_6D_5$ by $C_2H_4D^+$ in CF_4 at 720 Torr.

INC2, are quite close. Another interesting feature is that the extent of H/D scrambling is appreciably larger in the *m*- and *p*- than in the *o*-substituted product. In the case of $C_2D_4H^+$ ions, the scrambling is about five times smaller than in $C_2H_4D^+$ ions at 393 K, and falls below detection limits at lower temperatures. The ratio between unscrambled and scrambled products depends on the competition between process (2) and intracomplex alkylation, and obeys Equation (7), where k_s and k_2 are the rate constants for the H/D scrambling process (2) and for the alkylation within **INC2**, respectively.

$$\frac{[CF_3C_6X_4CY_2CXY_2]}{[CF_3C_6X_4CXYCY_3]} = \frac{2k_2}{k_s} + 1 \qquad (7)$$

Strictly, one should write three independent equations for *ortho*, *meta*, and *para* substitution, since it is apparent from Table 1 that their alkylation rates must be different, given the nonstatistical isomeric composition of the products; the extent of H/D scrambling is appreciably higher in the *m*- and *p*- than in *o*-substituted products. However, consideration of the weighted averages of k_2 and k_s instead simplifies the analysis substantially without introducing intolerably large errors, especially in view of the other approximations made in this study. Adopting this simplification, one obtains the following k_2/k_s ratios from the data in Table 1: 5.90 ± 0.15 (298 K), 5.33 ± 0.15 (315 K), 4.88 ± 0.20 (353 K), 4.32 ± 0.12 (393 K). All these values refer to the $C_2H_4D^+$ ion, whereas for the $C_2D_4H^+$ ion the only ratio available is 24 ± 4 (393 K).

Evaluation of the lifetime of INC2: The k_s values were calculated within the framework of transition state theory from the canonical expression of the unimolecular rate constant.

$$k_s = \sigma \left(\frac{kT}{h} \right) \exp \left(-\Delta G^{\ddagger}/kT \right) \qquad (7)$$

Table 2 reports $\Delta G^{\ddagger}$, obtained from the energies of ions **1** and **2** at 0 K computed at the G2 level, corrected to the four temperatures of interest by including the thermal contributions. The absolute entropies were derived from the molecular partition functions, calculated in turn from the scaled HF 6-31 G(d) harmonic frequencies and the moments of inertia of the species involved. By combining the computed k_s values with the k_2/k_s ratios reported in the preceding section, one can derive k_2 and hence the mean lifetime, $t = 1/k_2$, of the ethyl ion

within **INC2**, which corresponds to the mean lifetime of the complex. The lifetimes estimated at the temperatures of interest are 2.0×10^{-10} s (298 K), 1.2×10^{-10} s (315 K), 4.4×10^{-11} s (353 K), and 1.9×10^{-11} s (393 K). These values refer to alkylation by $C_2H_4D^+$, the only value available for alkylation by $C_2D_4H^+$ being 9.0×10^{-12} s (393 K). The scatter between the $C_2H_4D^+$ and $C_2D_4H^+$ results amounts to about 50 % and provides an (approximate) estimate of the internal consistency of the results from the approach followed in this study.

Reliability of the approach and comparison with related results: The major source of uncertainty concerns the rate constant k_s for process (2), in that the approach followed for its computation applies to *isolated* ethyl ions, whereas one deals instead with ions bound to $CF_3C_6X_5$ as **INC2**. The presence of the arene can conceivably affect the rate of process (2), for example by stabilizing ions **1** and **2** to a different extent by a differential solvation effect. Indeed, a hint of this effect can be found in the observation of less extensive H/D scrambling in the side chain of the products from *o*-substitution, a process where the ethyl ion can experience a closer interaction with the CF_3 group containing n-type centers. However, the relative stabilities of **1** and **2** are believed to be significantly affected only by close interaction with highly nucleophilic centers, such as O, Br, or I,[51] a situation quite different from that prevailing in **INC2**, which is characterized by a large, variable separation and a rapidly changing mutual orientation of its components, and by the presence of a neutral molecule whose principal nucleophilic system is highly delocalized. Thus, whereas the effects of such a peculiar microsolvation within **INC2** cannot be excluded, their influence on the estimated lifetime of the complex is probably not unduly large, and the error introduced is further reduced by taking into account the *averaged* k_2/k_s ratio, according to the procedure outlined above.

Another source of uncertainty worthy of mention is the possibility that the rate of process (2) is affected by tunnelling. In this connection, we note that the observed kinetic isotope effect (KIE) is relatively small, in contrast to the large KIE typical of processes where tunnelling plays a significant kinetic role.[52, 53] Furthermore, calculations performed with the Wigner equation[54] of the tunnelling correction to KIE, based on the scaled imaginary harmonic frequencies computed for the TS of process (2), namely 278.5i cm^{-1} for $C_2H_4D^+$ and 278.8i cm^{-1} for $C_2D_4H^+$, lead to correction
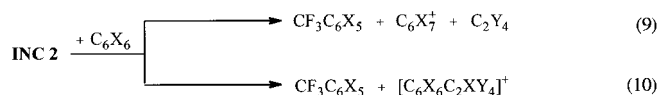
Table 2. Free energies of activation [kcal mol^{-1}] and rate constants [s^{-1}] for X scrambling in $C_2X_5^+$ ions (X = H,D).[a]

Reaction		298 K	315 K	353 K	393 K
$H_2C\overset{D}{\cdots}\overset{+}{\cdots}CH_2 \longrightarrow DH_2C-CH_2^+ \longrightarrow DHC\overset{+}{\cdots}CH_2$	$\Delta G^{\ddagger}$	5.70	5.70	5.68	5.67
	k_s	8.6×10^8	1.6×10^9	4.6×10^9	1.2×10^{10}
$D_2C\overset{H}{\cdots}\overset{+}{\cdots}CD_2 \longrightarrow HD_2C-CD_2^+ \longrightarrow DHC\overset{D}{\cdots}CD_2$	$\Delta G^{\ddagger}$	6.46	6.44	6.43	6.41
	k_s	2.4×10^8	5.0×10^9	1.6×10^9	4.6×10^9

[a] From the energies computed atr the G2 level, including the thermal energy contributions, and the absolute entropies of the species involved, see text.

factors close to unity at all temperatures investigated, suggesting that indeed tunnelling is not significant in this case.

As a preliminary test of the reliability of the results it is of interest to verify whether the **INC2** lifetimes from this study fall within the range defined by independent constraints. A *lower* limit, approximately 10^{-12} s, is set by the very definition of INCs as adducts whose components must undergo mutual rotation, and hence whose lifetimes must exceed the rotational period of the components. An *upper* limit to the **INC2** lifetime is set by the occurrence of bimolecular reactions, in particular with benzene, the base/nucleophile present at the highest concentration in the system. Owing to the high reactivity of benzene toward ethyl ion, processes such as (9) and (10) are expected to be fast, and at least (9) is likely to occur at a collision efficiency approaching unity. Utilizing the number density of C_6X_6 molecules and the collision rate constant from ADO theory or the trajectory algorithm,[55, 56] one obtains an upper limit of about 3×10^{-9} s for the **INC2** lifetime. It is encouraging, albeit certainly not conclusive, that the estimated values of the lifetimes fall within the (admittedly broad) range defined by the above limits.

$$\textbf{INC 2} \xrightarrow{+ \ C_6X_6} \begin{cases} \longrightarrow CF_3C_6X_5 \ + \ C_6X_7^+ \ + \ C_2Y_4 \qquad (9) \\ \\ \longrightarrow CF_3C_6X_5 \ + \ [C_6X_6C_2XY_4]^+ \qquad (10) \end{cases}$$

Finally, it is of interest to compare the present results with those from an independent approach, based on a high-pressure chemical activation technique.[26] The lifetime of the gaseous INC consisting of t-$C_4H_9XH^+$ (X = OH, Cl) and deuterated toluene was found to range from 5×10^{-11} to 1×10^{-10} s at temperatures from 273 to 315 K. These values are of the same order of magnitude as the lifetimes of **INC2** from this study, which range from 2×10^{-10} s at 298 K to 1.9×10^{-11} s at 393 K ($C_2H_4D^+$ ion) and to 9×10^{-12} s at 393 K ($C_2D_4H^+$ ion). At first sight, the close similarity of the lifetimes of two INCs consisting of widely different arene/electrophile pairs may appear surprising. However, it can be rationalized by taking into account the balance between the nucleophilic and the electrophilic reactivity of the arene/cation pairs making up the two INCs. Whereas $CH_3C_6H_5$ is a much better nucleophile than $CF_3C_6H_5$, t-$C_4H_9XH^+$ (X = OH, Cl) ions are much *weaker* electrophiles than $C_2H_5^+$ ions, and such opposite reactivity trends tend to cancel, which provides a reasonable explanation for the comparable lifetimes of the two gaseous INCs.[26]

Conclusions

The approach outlined in this paper has allowed approximate evaluation of the lifetimes of genuine INCs, previously characterized as the charged intermediates in the gas-phase Crafts–Friedel aromatic alkylation. The lifetimes obtained fall within the range defined by independent constraints and are comparable with those of gaseous INCs consisting of different arene/electrophile pairs, evaluated by an entirely different approach.[26]

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