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Brønsted versus Lewis Acid Reactivity of Gaseous Cations ($C_2H_5^+$, *i*-$C_3H_7^+$, HCO^+) toward Arenes

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Abstract: The reactivity of $C_2H_5^+$, *i*-$C_3H_7^+$, and HCO^+ ions, characterized by the simultaneous presence of acidic hydrogen(s) and of a carbon-centered electrophilic site, has been investigated with the aim of obtaining quantitative data on their competitive behavior as Lewis or Brønsted acids toward simple perdeuterated arenes. The reaction of the radiolytically formed cations in gaseous systems at a total pressure of ca. 700 Torr led to ethylated and isopropylated, but not formylated, products in addition to protonated products, i.e., the same substrates incorporating a ^{1}H atom on the aromatic ring. The NMR analysis of the reaction with toluene yielded ^{1}H incorporation/alkylation ratios of ca. 3.5 ($CH_5^+/C_2H_5^+$ reactant ions) and ca. 0.09 (*i*-$C_3H_7^+$ ions), which is suggested to reflect an intrinsic branching of two different reaction pathways, rather than competitive reaction channels of common intermediates. The dual behavior of ethyl cations emerged clearly in their reaction with benzene, where NMR and GC/MS analysis of the products from suitably labeled reactants led to a protonation/alkylation ratio of ca. 1.0. The protonation of toluene by $CH_5^+/C_2H_5^+$ shows a low positional selectivity and is followed by 1,2-hydrogen shifts having an estimated free energy of activation of ca. 8 kcal mol^{-1} at 37 °C.

Introduction

The reactivity behavior of alkyl cations toward arenes has long been the subject of active interest in gas-phase studies. In their initial studies Munson and Field determined the chemical ionization (CI) mass spectra of a large number of alkylbenzenes with methane as the reactant gas, reporting both protonation and ethylation reactions.[1] Since then, the protonation and alkylation reactions of aromatic substrates and the structural features of their ionic products have been investigated by mass spectrometric techniques.[2] However, one fundamental aspect, namely the site of proton or cation attachment to aromatic compounds, is still largely uncertain. A large body of gas-phase proton affinity (PA) data has been obtained from equilibrium studies, under conditions where the proton is attached to the thermodynamically favored site(s).[3] In these cases, substituent effects and correlations of PAs with core-binding energies have often been invoked to assist the assignment of ring versus substituent protonation. The assessment of which ring position(s) be involved is a more difficult problem to cope with. The determination of the relative stabilities of ortho-, meta-, and para-protonated monosubstituted benzenes has been addressed by theoretical calculations.[4] In some studies on the temperature dependence of equilibrium constants the site of ring protonation has been inferred from the values of the associated entropy changes. The observation of unusually large entropy changes has recently led to postulate a "dynamic" ionic structure for some protonated aromatic compounds.[5] However, most mass spectrometric studies suffer from two major limitations. The first is related to the definition of the "temperature" at which the reaction takes place in the single-collision regime frequently prevailing in mass spectrometric experiments,[6] where the method used to generate the reactant ions predetermines not only its energy content but also the overall energy level at which the reaction will be running and the excess energy ultimately deposited into the charged intermediates and products. A second problem concerns the structural assay of the latter ions which again often depends on their excess energy content, possibly allowing further isomerization and fragmentation processes, e.g., the reported study by MIKE and CID spectrometry of the structure and the isomerization mechanisms of gaseous arenium ions has a sampling time as long as 10 μs after their formation, which permits extensive isomerization before assay.[7]

A suitable method for the kinetic investigation of positive ions approaching thermal equilibrium with the gaseous environment is afforded by "high pressure" radiolytic[8] and nuclear decay[9] techniques. The electrophilic alkylation of arenes by cations such as $C_2H_5^+$ and *i*-$C_3H_7^+$ leading to neutral substitution products via arenium σ-complex intermediates has been studied in detail by the radiolytic technique.[10] However, whereas alkylated isomeric products from cation attachment are easily detectable, e.g., by GC or GC/MS analysis of the neutral products mixtures, the radiolytic technique is blind to proton attachment processes to the extent that they leave the substrate unchanged, i.e., unless isotopically labeled reactants are used, deprotonation of the arenium ions regenerates the starting substrate. In previous studies, radiolytic and nuclear decay techniques have been applied to the study of tritium atom incorporation on toluene following however reactions promoted by $^3HeT^+$ and D_2T^+ ions, which are far too energetic to allow any correlation of the observed tritium distribution with the pattern of kinetic attack.[11] Since the elementary

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process of proton transfer to aromatic molecules is still largely unknown, we have focussed our attention on proton transfer to simple arenes (benzene, toluene, *o*-xylene), either by pure Brønsted acids or from alkyl cations which display both Brønsted and Lewis acid reactivity (HCO^+, $CH_5^+/C_2H_5^+$, *i*-$C_3H_7^+$). The reactions were studied by determining the extent of H incorporation[12] into the perdeuterated substrates. The NMR technique, recently introduced as a tool for the characterization of neutral products of ion–molecule reactions,[13] has been exploited to obtain the pattern of the intramolecular H distribution.

Experimental Section

Materials. The perdeuterated compounds used as substrates or as NMR standards, benzene-d_6, toluene-d_8, *o*-xylene-d_{10}, *p*-dichlorobenzene-d_4, with stated isotopic purities of >99.96%, >99.96%, >99%, and 99%, respectively, were purchased from Aldrich Chimica S.r.l. or Fluka Chemie AG. The same firms supplied the solvents $(CD_3)_2CO$ and CD_2Cl_2. [$^{12}C_6$]Benzene (99.9%) and C_2D_4 (99%) were purchased from Cambridge Isotope Laboratories, Inc. Isopropylbenzene-d_{12} was prepared from isopropyl alcohol-d_8 and benzene-d_6 by mixing the reagents in the presence of D_2SO_4. The unlabeled products used as gas chromatographic standards were commercial products or were prepared according to established procedures. H_2, CH_4, CO, and C_3H_8 were research grade gases from Matheson Co. with a stated purity in excess of 99.95% and were used without further purification.

Procedure. The gaseous samples were prepared by routine vacuum line procedures as previously described in detail.[10] In a typical experiment, a few milligrams of the aromatic substrate, sealed into a fragile glass ampoule, was introduced into a 1-L Pyrex vessel, equipped with a break-seal tip and connected to the vacuum line by another arm. After thoroughly outgassing, the vessel was filled with the gaseous components (ca. 700 Torr bulk gas and 10 Torr O_2), cooled to the liquid nitrogen temperature, and sealed off. The aromatic substrate was let to evaporate after breaking its ampoule, and the vessel was let to equilibrate at the irradiation temperature, 37 °C unless stated otherwise. The irradiations were carried out in a 220 Gammacell (Nuclear Canada Ltd.) at total doses ranging from 5×10^4 Gy to 10×10^4 Gy at the dose rate of ca. 1×10^4 Gy h^{-1}. The radiolytic product mixture was extracted by freezing the vessel in liquid nitrogen and then washing its inner walls with a deuterated solvent ($(CD_3)_2CO$ or CD_2Cl_2) with repeated freeze–thaw cycles. The analysis of measured aliquots of the resulting solution was carried out by GC and GC-MS using a Hewlett Packard 5890 gas chromatograph equipped with a FID unit or with a HP mass selective detector model 5970B. The capillary columns performing satisfactory separations of the isomeric products were the following: (i) a 30-m long, 0.32-mm i.d. fused silica column with a 1-μm film of dimethylpolysiloxane phase (Supelco SPB-1); (ii) a 60-m long, 0.75-mm i.d. borosilicate glass column coated with a 1-μm film of Carbowax 20M phase; (iii) a 50-m long, 0.20-mm i.d. fused silica column, coated with a 0.5-μm cross-linked methylsilicone film (HP PONA column). The mass detector, operated in the selected ion mode (SIM), was specifically used to determine the extent of D incorporation into ^{13}C-depleted benzene ([$^{12}C_6$]benzene 99.9%) following its reaction with deuterated ions.

The same solutions, without further workup, were also assayed by NMR spectrometry to analyze the H content and distribution into the substrate and its alkylation products, as described in the following section. The correct assignment of the ^1H NMR signals, their frequencies, and relative intensities were checked in several cases by isolating individual products and the substrate itself by preparative GC using a 4-m long column packed with Carbowax 20M (10%)/KOH (2%) on Supelcoport. In this way it was ascertained that there were no overlapping peaks in the spectral regions of interest and a sensible gain in the signal-to-noise ratio was achieved, having removed the large signals of undeuterated compounds, e.g., the bulk gas partially soluble in the extraction solution. The NMR spectra were recorded on a Varian XL 300 instrument with a H probe operating at 299.9 MHz. The deuterium signal of the solvent was used as the lock and TMS as internal reference for the assignments of chemical shifts. All the spectra have been recorded using a sweep width of 4000 Hz, 25° flip angle and a repetition time of 10 s. On the average, 4000 scans were enough to ensure a good signal-to-noise ratio. The assessment of the H incorporation and its positional distribution into the substrate and its alkylation products required the preliminary precise knowledge of the chemical shifts of the aromatic hydrogen atom into otherwise perdeuterated arenes in the solvented used. Table I summarizes these data, anchored to the known H chemical shifts of toluene in neat toluene-d_8.[14] The proton chemical shifts of $CD_3C_6D_4H$ displayed a remarkable sensitivity to the solvent with meta and para H's reverting their resonance positions in going from neat toluene-d_8 to $(CD_3)_2CO$ or CD_2Cl_2 solution. The quantitation of the H incorporation into the substrate with respect to the alkylation products was achieved by using *p*-dichlorobenzene-d_4 as the calibration standard, owing to the resonance frequency of its residual proton falling closely outside the spectral region of interest. The relative response to the GC detector and the integral ratio of the NMR signals were obtained from a weighted mixture of the standard and the substrate arene dissolved in the NMR solvent. This solution represented the reference against which the radiolytic solutions were compared to check in the first place if and to what extent the H atoms in the recovered substrate exceeded the residual fraction already present in the unreacted substrate. Figure 1 shows the integration of a typical spectrum of the aromatic protons of $CD_3C_6D_4H$, recovered from the gas-phase radiolytic systems, from which the % H distribution on the ring positions was obtained.

Table I. NMR Data on Aromatic Proton in Otherwise Perdeuterated Arenes

arene	δ (ppm) 2	δ (ppm) 3	δ (ppm) 4	$^4J_{HD}$ (Hz)	solvent
MePh-d_7	7.188	7.310	7.229		toluene-d_8
MePh-d_7	7.176 (t)	7.239 (m)	7.140 (m)	1.1	$(CD_3)_2CO$
MePh-d_7	7.367 (t)	7.435 (m)	7.337 (m)	1.1	CD_2Cl_2
EtPh-d_9	7.224 (t)	7.285 (m)	7.176 (m)	1.1	$(CD_3)_2CO$
i-PrPh-d_{11}	7.241 (t)	7.275 (m)	7.155 (m)	1.1	$(CD_3)_2CO$
o-xylene-d_9	7.111 (t)	7.060 (m)		1.1	$(CD_3)_2CO$
p-dichlorobenzene-d_3	7.438 (t)	7.438 (t)		1.3	$(CD_3)_2CO$

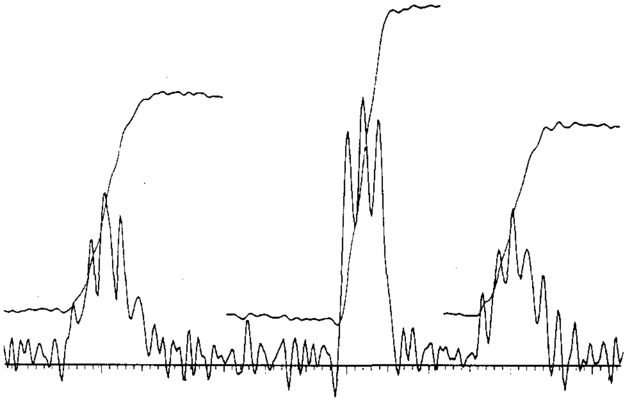

Figure 1. NMR spectrum of the aromatic protons of $CD_3C_6D_4H$ formed from $CD_3C_6D_5$ (1.7 Torr) in the $CH_4/O_2/(CD_3)_2CO$ 230:3:1 gaseous mixture at 700 Torr, 37 °C.

Results

Table II summarizes the results concerning alkylated and protodedeuterated products from the gas-phase reaction of perdeuterated arenes (benzene, toluene, *o*-xylene) with charged electrophiles ($CH_5^+/C_2H_5^+$, *i*-$C_3H_7^+$, HCO^+). The last entry illustrates an experiment designed to investigate the reactivity of $C_2D_4H^+$ ions from the protonation of perdeuterated ethylene toward ^{13}C-depleted benzene. The table shows the isomeric composition of alkylated and protodedeuterated products and their relative yields. The absolute radiolytic yields, measured by the G_{+M} values, are not reported being of less mechanistic significance as they depend on specific factors, e.g., the growth of radiolytic products, which may change from system to system, varying with the total pressure and the radiation dose. Anyhow, the overall G_{+M} values (μmol J^{-1}) were close to the known G_{+M} values of the reactant cations and showed the expected decreasing trend with increasing concentrations of acetone, a base/nucleophile capable of intercepting the charged electrophiles. The total irradiation dose was chosen as a compromise between the necessity to obtain

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[12] The symbol H is used for protium (^1H) and D for deuterium (^2H) throughout this paper.

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Table II. Gas-Phase Reaction of Cationic Electrophiles with Perdeuterated Arenes

entry no.	system composition,[a] Torr						reagent ion(s)	alkylated and protodedeuterated products							
	substrate ArD		bulk gas		additive(s)			Ar–R isomeric compostn,[b] %			% H incorprtn in the Ar–R products	ArH positional distribtn of H,[b] %			ArH/ArR yield ratio (ratio of H incorprtn to alkylation)[c]
								2	3	4		2	3	4	
1	C_6D_6	(2.0)	CH_4	(700)			CH_5^+, $C_2H_5^+$ = R^+		na		16[d]		na		5.0
2	C_7D_8	(1.7)	CH_4	(680)			CH_5^+, $C_2H_5^+$ = R^+	45	32	23	31	48	23	29	4.0
3	C_7D_8	(1.5)	CH_4	(700)	$(CD_3)_2CO$	(0.8)	CH_5^+, $C_2H_5^+$ = R^+	43	33	24	13	44	30	26	3.2
4	C_7D_8	(1.7)	CH_4	(680)	$(CD_3)_2CO$	(3.0)	CH_5^+, $C_2H_5^+$ = R^+	42	35	23	*e*	44	35	21	4.0
5	C_7D_8	(1.7)	CH_4	(690)	$(CD_3)_2CO$	(6.0)	CH_5^+, $C_2H_5^+$ = R^+	39	39	22	*e*	44	36	20	3.0
6	C_7D_8	(4.4)	CH_4	(700)	C_6H_6	(4.0)	CH_5^+, $C_2H_5^+$ = R^+	43	33	24	31	51	20	29	*f*
7	*o*-$(CD_3)_2C_6D_4$	(2.0)	CH_4	(700)			CH_5^+, $C_2H_5^+$ = R^+		45	55	24		49	51	4.4
8	C_6D_6	(1.4)	C_3H_8	(700)			*i*-$C_3H_7^+$ = R^+		na		18[g]		na		≤0.05
9	C_7D_8	(1.9)	C_3H_8	(680)			*i*-$C_3H_7^+$ = R^+	46	31	23	14	47	26	27	0.09
10	C_7D_8	(2.0)	C_3H_8	(690)	*h*		*i*-$C_3H_7^+$ = R^+	43	34	23	22		*i*		0.20
11	C_7D_8	(0.3)	C_3H_8	(70)			*i*-$C_3H_7^+$ = R^+	45	35	20	28		*i*		0.23
12	C_7D_8	(1.5)	C_3H_8	(690)	$(CD_3)_2CO$	(1.5)	*i*-$C_3H_7^+$ = R^+	46	28	26	4		*i*		0.09
13	*o*-$(CD_3)_2C_6D_4$	(1.8)	C_3H_8	(680)			*i*-$C_3H_7^+$ = R^+		60	40	15		*i*		*i*
14	C_7D_8	(0.8)	H_2 (680), CO (20)				HCO^+					49	23	28	*j*
15	$^{12}C_6$-C_6H_6	(2.6)	CH_4	(710)	C_2D_4	(10)	CH_5^+, $C_2H_5^+$, $C_2D_4H^+$		na[k]				na		1.1[l]

[a] The 1-L vessel always contained O_2, 10 Torr. [b] Not applicable (na) for C_6D_6 and $^{12}C_6$-C_6H_6. Standard deviation of data ca. 2%. [c] Standard deviation ca. 10%. [d] The H distribution in the EtC_6HD_4 product was found to be 59% ortho, 6% meta, and 35% para. [e] Below detection limit (ca. 2%). [f] This ratio, obtainable by NMR analysis of the product mixture, could not be determined in this experiment because of the strong signal of C_6H_6. Instead, from this experiment, the toluene substrate was isolated by preparative GLC to be examined by NMR in the specific search of *double* ring H incorporation. However, if any $CD_3C_6H_2D_3$ isomers are formed, they would account for less than 10% with respect to $CD_3C_6HD_4$. In this same experiment, the ethylation product of C_6H_6 was found to incorporate deuterium on the aromatic ring by GLC-MS analysis (EtC_6H_5, 49%; EtC_6H_4D, 47%; $EtC_6H_3D_2$, 4%). [g] The H distribution in the *i*-PrC_6HD_4 product was found to be 58% ortho, 6% meta, 36% para. [h] Irradiation carried out at 120 °C. [i] The yield of ArH is too low to give data within the stated given confidence limits. [j] Specific search for H incorporation in the methyl group of toluene revealed a negligible contribution (≤6% with respect to ring H incorporation). [k] The $C_6H_5C_2D_4H/C_6H_5C_2H_5$ yield ratio is 1.2. [l] This value corresponds to the $C_6H_5D/C_6H_5C_2D_4H$ yield ratio, multiplied by the 5/4 statistical factor arising from the incomplete deuteration of the reacting ethyl cation.

adequate amounts of products for NMR analysis and the need to minimize the extent of unwanted reactions, which might alter the primary, kinetically significant product pattern.

The Alkylation Products. The carbenium ions, $C_2H_5^+$ (in CH_4) and $C_3H_7^+$ (in C_3H_8), yield alkylated arenes whose isomeric distribution is given in Table II. The presence of acetone, a fairly strong base, added in a few experiments ensures that the observed isomeric distributions approach the kinetic pattern of the electrophilic attack because rapid deprotonation prevents further isomerization of the ionic intermediates. The reaction of the ethyl cation with toluene in the presence of acetone (6 Torr) shows a distribution close to the 40:40:20 statistical o:m:p ratio. The *i*-$C_3H_7^+$ ion shows a positional selectivity characterized by a meta/2 para ratio of ca. 0.5, in the presence of 1.5 Torr acetone, in agreement with previous studies.[10b,c] We have found that the alkylation process is frequently accompanied by H incorporation into the aromatic ring, to an extent which largely exceeds the initial amount of protium in the starting substrate. The occurrence of this H incorporation was detected first by NMR spectrometry of the crude solutions from the radiolysis and was later confirmed by the NMR analysis of the individual products isolated by preparative GC. The mass spectra of the alkylated products displayed intensities of both the molecular ion and the charged fragments consistent with the presence of protium, whose fraction corresponded to that obtained from the NMR integral ratio of the aromatic versus the aliphatic protons. Both techniques concur in excluding any significant deuterium incorporation into the alkyl group, thus disproving that isotope mixing between the deuterated arene and the attacking alkyl cation can lead to ring protonation. The fraction of H incorporated into the ring of the ethyltoluenes formed in methane (31%) decreases in the presence of added $(CD_3)_2CO$, while 4.0 Torr C_6H_6 leaves this fraction unchanged. The fraction of H incorporation in the ring of the cymenes formed in propane is comparably smaller (14%), becomining negligible when $(CD_3)_2CO$ is added but shows an increase with lower propane pressures or higher temperatures. The distribution of H in the ring, which could be established in the products from benzene-d_6, i.e., ethylbenzene and isopropylbenzene, privileged strongly the ortho and para positions in both products (EtPh 59% ortho, 6% meta, 35% para; *i*-PrPh 58% ortho, 6% meta, 36% para).

H Incorporation into Perdeuterated Substrates. The last two columns of Table II report the distribution of H atoms in the ring positions of the starting substrate after the radiolysis and the ratio between the yields of the products from H incorporation and alkylation. This ratio was deduced from the NMR integral ratio between the aromatic protons of the substrate and the alkyl protons of the alkylated products, corrected by their number. These data needed no correction for the fraction of H atoms originally present as an isotopic impurity in the substrates, because such background contribution was negligible under all circumstances, except in the case of *o*-xylene. The extent of H incorporation by the substrate was markedly different in the gaseous systems examined. Thus, whereas the ions from CH_4 and from the H_2/CO 34:1 mixture led to the highest H incorporation, the ions from propane were by far less efficient. In the latter system, no reliable results could be obtained from deuterated *o*-xylene, the substrate with the lowest degree of isotopic purity.

The ring distribution of H in the toluene recovered from the neat methane system is close to that obtained in the H_2/CO mixture but shows a trend of decreasing para/meta ratio in the presence of increasing amounts of $(CD_3)_2CO$. In those experiments where the substrate had been isolated by preparative GC and analyzed by NMR, the positional H distribution was confirmed to be the same as in the crude solutions, though the purification procedure caused some loss of the arene. A specific search aimed at the detection of any conceivable products from double H incorporation, i.e., of $MeC_6D_3H_2$, failed, establishing a higher limit of ca. 10% to the presence of such products. The latter finding holds under all conditions reported in Table II, including the reaction in methane with added C_6H_6 and in the H_2/CO mixture. No evidence for H incorporation into the methyl group emerged either. The toluene recovered from the reaction in H_2/CO could be most carefully checked. In this system HCO^+ ions react exclusively by proton transfer and yield clean product mixtures, whose analysis in CD_2Cl_2, revealed no significant H incorporation into the methyl group (≤6%).

The H atoms incorporated into *o*-xylene in CH_4 are about equally distributed on the 3- and 4-positions. As with toluene, whereas the H distribution from the CH_4 and H_2/CO systems at ca. 1 atm is very similar, the meta position seems slightly more favored in propane. The low H incorporation in propane prevented a reliable measurement of its ring distributions, except when the substrate was isolated from two or more separate runs and the combined fractions analyzed by NMR.

The Ratio of H Incorporation to Alkylation. The ratio of H incorporation into the substrate to its alkylation in methane systems (ca. 1 atm) ranges from 3.0 to 5.8 for all substrates investigated. In the case of toluene, the presence of increasing amounts of $(CD_3)_2CO$ causes no appreciable changes in this ratio, which remains constant at 3.5 ± 0.5. No distinct trend emerges from the comparison of the values obtained for the three substrates: benzene (5.0), toluene (3.5), and *o*-xylene (4.4). The addition of C_2D_4 1.4 mol% in CH_4 (last entry in Table II) leads to the formation of $C_6H_5C_2D_4H$ and $C_6H_5C_2H_5$ in the 1.2 yield ratio and to the incorporation of a D atom into benzene. The $C_6H_5D/C_6H_5C_2D_4H$ yield ratio was determined by GC/MS, using weighted benzene/ethylbenzene calibration mixtures. Mass spectral analysis showed that the four D atoms of ethylbenzene-d_4 were statistically distributed in the 1- and 2-positions of the ethyl group,[15] while the extent of D incorporation into benzene was afforded by the increased intensity of the isotopic peak at m/z 79. The latter determination was allowed by the diminished content of ^{13}C in the benzene used.

The ratio of H incorporation versus isopropylation of toluene measured in propane (ca. 1 atm) is characterized by the value of 0.09, not affected by the addition of 1.5 Torr $(CD_3)_2CO$. However, both lowering the C_3H_8 pressure down to 70 Torr and increasing the temperature from 37 °C up to 120 °C brings about an increase of the ratio to 0.20 and, respectively, to 0.23. The ratio of H incorporation versus alkylation for the different substrates in propane could not be determined, owing to the low yields of H incorporation; an upper limit of 0.05 was obtained for benzene, while, in the case of *o*-xylene, the increase of H content following radiolysis was too low to provide meaningful data.

Discussion

The Ionic Reagents and Their Gaseous Environment. Since the comparative study of the Brønsted versus Lewis acid reactivity of selected gaseous cations was the primary goal of our investigation, we sought to generate the cations of interest as the main ionic species in a poorly solvating gaseous environment, where their inherent reactivity is not affected by counterions nor by formation of strong association complexes with the medium. Secondary propyl cations formed by the γ-radiolysis of propane fulfill this requirement. In fact, gaseous $i\text{-}C_3H_7^+$ ions are the major ionic species obtained from the radiolysis of propane, with a G_{+M} value of ca. 0.3 μmol J^{-1}.[16] They are formed either by direct dissociative ionization of propane or by exothermic hydride abstraction by fragment ions, e.g., $C_2H_5^+$ and $C_3H_5^+$, from C_3H_8. The $i\text{-}C_3H_7^+$ ions, whose excess energy content, related to their formation processes, is rapidly removed by collisions with propane, ultimately form an electrostatic association complex with C_3H_8.[17] The interaction of $i\text{-}C_3H_7^+$ ions with selected arenes (benzene, toluene, and *o*-xylene) may promote both proton transfer and alkylation, according to the exothermic processes whose energetics are summarized in Table III. Ethyl ions are formed from the radiolysis of methane, together with CH_5^+ ions, their G_{+M} values being ca. 0.09 and 0.19 μmol J^{-1}, respectively.[18] Thus, $C_2H_5^+$ ions are not the only nor the predominant cationic species.[19] As in the case of $i\text{-}C_3H_7^+$ ions in propane, CH_5^+ and $C_2H_5^+$ ions form association complexes with methane to an estimated extent of 80% and 25%, respectively.[20] With the aim to figure out the kinetic role of ethyl cations alone, a C_2D_4 (1.4 mol%) in CH_4 gaseous mixture has been used, where the CH_5^+ and $C_2H_5^+$ ions primarily formed may protonate deuterated ethylene forming $C_2D_4H^+$ ions.

The next higher homologue, $t\text{-}C_4H_9^+$, was not included in this study because thermochemical constraints prevent proton transfer to the selected arenes, while its alkylating reactivity has thoroughly been examined.[21] At the other extreme, HCO^+ is a purely protonating reactant, obtained from the ionization of a dilute solution of CO in H_2. Irradiation of H_2, the bulk component of the gas, is known to yield H_3^+, an exceedingly strong Brønsted acid, according to well-established processes.[22] H_3^+ can exothermically accomplish both O-protonation and C-protonation of CO, yielding excited formylium and isoformylium ions.[23] Following thermalization by a large number of unreactive collisions with the bath gas and proton exchange with CO molecules, the ensuing ground-state HCO^+ ions, associated to a CO molecule,[24] react exclusively as proton donors toward the selected arenes.

The reaction environment consists of gases with stated purity >99.95% in which minute concentrations of the aromatic substrates (typically ca. 0.3 mol%) are present. At such high dilution, which is used to minimize direct radiolysis of the aromatics, the presence of impurities in the bulk gas, e.g., H_2O, may have significant effects despite their low concentration (<0.05 mol %). The formation of radiolytic products from the bulk gas must also be considered, e.g., H_2O, low molecular-weight olefins, alcohols peroxides, and carbonyl compounds from CH_4 and C_3H_8/O_2 mixtures.[25] Their concentration increases with the radiation dose to a total amount not exceeding 0.06 mol % under the experimental conditions adopted. Thus, trace quantities of neutrals are present in the gaseous medium and may play a role in the reaction patterns under study, an effect which can be controlled by deliberate addition of known amounts of more reactive compounds. On the other hand, the presence of O_2 in large excess over the aromatic substrate, which triggers the formation of oxygenated compounds, is needed to inhibit the contribution from radical pathways to the observed products in all systems.

Table III summarizes the thermochemical data concerning the protonation and the alkylation reactions by the gaseous cations on unlabeled arenes. The values, which refer to isotopically unlabeled species, will be taken as appropriate for the perdeuterated arenes as well. In fact, it has been observed that CD_3 for CH_3 substitution affects little, if at all, proton-transfer equilibria, e.g., the PA of $C_6H_5CD_3$ is the same as that of $C_6H_5CH_3$ within experimental error.[26] The same may not hold when D replaces H on the C atom undergoing reaction and hybridization change, but the energy differences involved are expected to be small with respect to the uncertainties of the thermochemical data. Finally, it must be added that the thermochemical data reported pertain to isolated ions, whereas, as mentioned above, at the

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(15) This analysis was allowed by the negligible scrambling of H/D atoms in the ion source fragmentation of a methyl group from ionized labeled ethylbenzene: Grotemeyer, J.; Grützmacher, H.-F. *Org. Mass Spectrom.* **1982**, *17*, 353.

(16) (a) Ausloos, P.; Lias, S. G. *J. Chem. Phys.* **1962**, *36*, 3163. (b) Lias, S. G.; Ausloos, P. *J. Chem. Phys.* **1962**, *37*, 877. (c) Sandoval, I. B.; Ausloos, P. *J. Chem. Phys.* **1963**, *38*, 2452.

(17) Sunner, J. A.; Hirao, K.; Kebarle, P. *J. Phys. Chem.* **1989**, *93*, 4010.

(18) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341.

(19) The attainment of an ionic population consisting exclusively of $C_2H_5^+$ ions is not straightforward. Addition of C_2H_6 to CH_4 would not solve the problem since formation of protonated ethane $CH_5^+ + C_2H_6 \rightarrow CH_4 + C_2H_7^+$ is known to occur with $\Delta H^\circ = -12$ kcal mol^{-1} and the decomposition $C_2H_7^+ \rightarrow H_2 + C_2H_5^+$ does not take place below 40 °C, see: Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119. Furthermore, $C_2H_5^+$ may react with ethane, producing a complex mixture of alkylating and protonating ions of varying strengths: Munson, M. S. B.; Franklin, J. L.; Field, F. H. *J. Phys. Chem.* **1964**, *68*, 3098. For these reasons, we preferred to study the behavior of the $C_2H_5^+/CH_5^+$ mixture, containing a well-defined ratio of the two ions arising from radiolysis of pure methane.

(20) (a) Hiraoka, K.; Kebarke, P. *J. Am. Chem. Soc.* **1975**, *97*, 4179. (b) Hiraoka, K.; Kebarke, P. *Can. J. Chem.* **1975**, *53*, 970.

(21) Cacace, F.; Ciranni, G. *J. Am. Chem. Soc.* **1986**, *108*, 887, and references therein.

(22) (a) Ausloos, P.; Lias, S. G. *J. Chem. Phys.* **1964**, *40*, 3599. (b) Ausloos, P. *Prog. React. Kinet.* **1969**, *5*, 113.

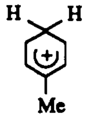
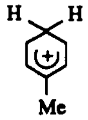
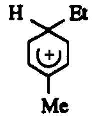
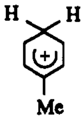
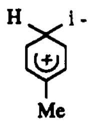
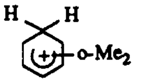
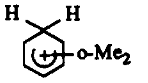
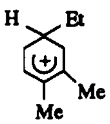
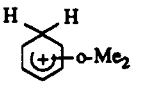
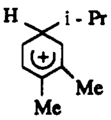
(23) McMahon, T. B.; Kebarle, P. *J. Chem. Phys.* **1985**, *83*, 3919.

(24) Keese, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

(25) Spinks, J. W. T.; Woods, R. J. *Introduction to Radiation Chemistry*; Wiley: New York, 1990; pp 227 and 370.

(26) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1977**, *99*, 4198.

Table III. Estimated Thermochemical Data[a]

substrate	reactant ion	product ion	$\Delta H°$, kcal mol^{-1}
benzene	CH_5^+	$C_6H_7^+$	−49.7
benzene	$C_2H_5^+$	$C_6H_7^+$	−19
benzene	$C_2H_5^+$		−43
benzene	i-$C_3H_7^+$	$C_6H_7^+$	−1.8
benzene	i-$C_3H_7^+$		−25
toluene	HCO^+		−48
toluene	CH_5^+		−58
toluene	$C_2H_5^+$		−27
toluene	$C_2H_5^+$		−52
toluene	i-$C_3H_7^+$		−10
toluene	i-$C_3H_7^+$		−33
o-xylene	CH_5^+		−62
o-xylene	$C_2H_5^+$		−31
o-xylene	$C_2H_5^+$		−55
o-xylene	i-$C_3H_7^+$		−14
o-xylene	i-$C_3H_7^+$		−37

[a] Thermochemical data for neutral species: (i) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London 1970. (ii) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. The formation enthalpies of the ions: (iii) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. The PA of the alkylated ring position of the relevant arene was taken to be equal to that of the same position in the corresponding arene.

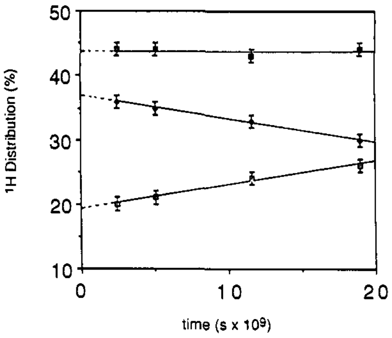
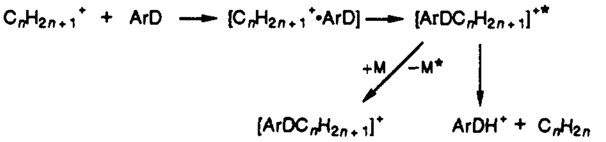


Figure 2. ^1H Distribution ((□ ortho; (♦) meta; (▣) para) on the ring positions of perdeuterated toluene after reaction in CH_4 (700 Torr)/O_2 (10 Torr)/$(CD_3)_2CO$ (0.8–6.0 Torr) versus the arenium ion lifetime, calculated from $k_{coll}(C_7D_8H^+$ + acetone) using ADO theory.

relatively high pressure typical of radiolytic systems the reactant ions are associated with bath-gas molecules, as probably are the charged products too. The overall effect of such association processes is to decrease the exothermicity of the reaction with respect to that calculated for unsolvated species, in that, whereas the reactant ions can be strongly bound to the bath-gas molecules, e.g., the binding energy of the i-$C_3H_7^+{\cdot}C_3H_8$ complex is 13.6 kcal mol^{-1},[17] the product arenium ions are less strongly associated, if at all, owing to their much greater charge delocalization. In any case, the association of the reactant ion with a bath-gas molecule contributes to remove the excess internal energy imparted to the arenium ions by the exothermicity of their formation process, since the molecule bound to reactant ion may bounce off with excess kinetic energy from the products side.

The Alkylation Reaction. The reactivity of $C_2H_5^+$ and i-$C_3H_7^+$ ions as alkylating agents under CI and radiolytic conditions has been the subject of extensive previous investigations[10] and will not be further discussed. Suffice it to say that both ions, more markedly $C_2H_5^+$, are characterized by a high reactivity, low regioselectivity, and a high exothermicity of their addition reaction to the aromatic substrates, congruous with the observed isomeric composition of the Ar–R products shown in Table II. At the relatively high pressure of radiolytic systems, aromatic substitution by gaseous cations involves the intermediacy of a σ-complex following the preliminary formation of an electrostatically bound collision complex between the reactant ion and the substrate.[8a] Unless the excess energy content imparted to the addition σ-complex by its exothermic formation process is rapidly removed by thermalyzing collisions, fragmentation may take place, the lowest energy pathway leading to the protonated arene and neutral alkene (eq 1). It is therefore conceivable that protonation may



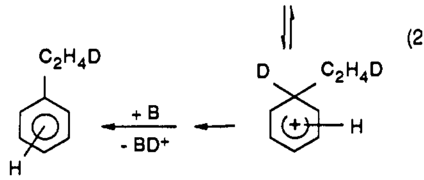
$$C_nH_{2n+1}^+ + ArD \longrightarrow [C_nH_{2n+1}^+{\cdot}ArD] \longrightarrow [ArDC_nH_{2n+1}]^{+*} \xrightarrow[-M^*]{+M} [ArDC_nH_{2n+1}]^+ ; \quad [ArDC_nH_{2n+1}]^{+*} \longrightarrow ArDH^+ + C_nH_{2n} \qquad (1)$$

derive, at least partly, from the fragmentation of the same σ-complex intermediates whose collisional deactivation yields the alkylation products, the branching between fragmentation and deactivation depending on the rate of removal of excess internal energy. In fact, the fragmentation–protonation channel is known to prevail at the low pressures typical of CI mass spectrometry, i.e., under conditions less favorable for quenching excited intermediates.

Isotope Exchange in the Alkylation Products. The use of labeled aromatics has revealed an otherwise hidden feature of the alkylation reaction. Both ethylated and isopropylated arenes formed in the radiolytic experiments display some degree of H incorporation into the aromatic ring which is however *not* accompanied by a corresponding D incorporation into the alkyl group. This emerges from the data in Table II, showing the extent of H incorporation into the alkylated products. The H incorporation into the aromatic ring may be traced either to a (unimolecular) process occurring within the collision complex between the alkyl cation and the arene or to a (bimolecular) isotope exchange reaction following the formation of the σ-complex and involving a proton donor species. The lack of a corresponding D incorporation into the alkyl group speaks against unimolecular mechanisms, e.g., isotope exchange between a D atom of the ring and a H atom of the alkyl group prior to, or concerted with, C–C bond formation, as exemplified in eq 2. The mechanism depicted in eq 2 would

$$C_2H_5^+ + C_6D_6 \rightarrow$$

$$[C_2H_5^+ \cdot C_6D_6] \rightleftarrows [C_2H_4 \cdot C_6D_6H^+] \rightleftarrows [C_2H_4D^+ \cdot C_6D_5H]$$



(2)

also predict a nearly uniform H distribution in the ring positions of ethylbenzene, in sharp contrast with the appreciable selectivity (59% ortho, 6% meta, and 35% para) found experimentally. Furthermore, the closely similar H distribution (58% ortho, 6% meta, and 36% para) found in isopropylbenzene indicates that the specific nature of the alkyl group has little effects. The experimental results are better explained by a H/D exchange process occurring *after* the formation of the arenium ion, e.g., eq 3.

$$RC_6D_6^+ + XH \longrightarrow [RC_6D_6^+ \cdot XH] \rightleftarrows [RC_6D_5 \cdot XHD^+] \rightleftarrows [RC_6D_5H^+ \cdot XD]$$

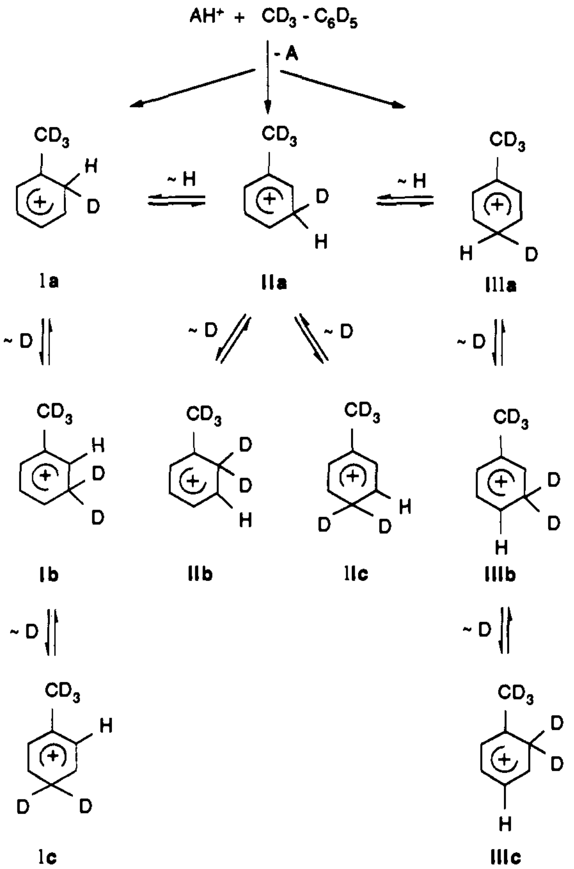
$$RC_6D_4H \xleftarrow[-BD^+]{+B} \xleftarrow{-XD} RC_6D_5H^+ + XD \quad (3)$$

Though not deliberately introduced into the gaseous systems, species XH, capable of promoting partial H incorporation into the alkylation products, may be present as traces as referred to in the above section. Although most of these XH compounds are unable to deprotonate the arenium ions because of their inadequate basicity, they still may undergo sequential H/D transfer. In fact, isotope exchange reactions within a collision complex, allowed by the electrostatic energy released in the association of the ion with the polar molecule, have been observed both by ion cyclotron resonance and by high-pressure mass spectrometry.[27] In this work, evidence for such processes has been found as well at a much higher pressure than prevailing in mass spectrometric studies.

The interpretation of the partial, highly regioselective H incorporation into the alkylated products provided by eq 3 is consistent with its suppression when a strong deuterated base, $(CD_3)_2CO$, is added. $(CD_3)_2CO$ ensures fast deprotonation of the arenium ions, minimizing the time allowed to their encounters with trace proton donor species. It should be noted that the mere presence of H atoms in a species whose PA value is close to that of alkylated arenes is not sufficient to qualify such species as an efficient promoter of the H/D exchange. This is apparent from entry no. 6, Table II, where the presence of added C_6H_6 does not affect the extent of H incorporation into the ring of the ethylated products from toluene-d_8.[28]

The H Incorporation Reaction. The dual reactivity behavior of alkyl cations as alkylating and protonating agents, well-known in CI mass spectrometry, emerges as well at the much higher pressures typical of the present radiolytic reactions. Proton transfer from carbenium ions, either direct or possibly upon fragmentation of alkylated intermediates, suggested in the above section, and from pure Brønsted acids to perdeuterated toluene initially yields a mixture of *o*-, *m*-, and *p*-H-toluenium-d_8 ions, ortho and para σ-bonded arenium ions being recognized as the most stable structures of protonated toluene[2] (Scheme I). Ions I–III may undergo H shifts and D shifts governed by (i) thermodynamic factors, (ii) kinetic intrinsic barriers, and (iii) kinetic isotope effects. The first effect is expected to favor conversion of meta σ-complexes into the more stable ortho and para isomers. As with factor (ii), an Arrhenius activation energy $E_a = 10 \pm 1$ kcal mol^{-1} and a preexponential factor of $10^{15.9\pm1.6}$ s^{-1}, corresponding to a free energy of activation of 5.7 kcal mol^{-1} at 298 K, for the degenerate 1,2-hydrogen shift in benzenium ions were obtained by Olah et al. by dynamic NMR in superacid solution.[29] Gas-phase data are much less conclusive. In their recent study on the thermodynamics of proton-transfer reactions in arene–arenium ion systems, Mason et al. reported an activation barrier ≤5.5 kcal mol^{-1} for the benzenium system, related to the existence of a *dynamic* upper state whereby a proton is regarded as free to migrate over the six ring positions.[5b] Evaluation of the kinetic barriers for hydrogen shifts in benzenium and toluenium ions could not be achieved in the mass spectrometric study of the isomerization of metastable $C_6H_7^+$ and $C_7H_9^+$ ions.[30] As to factor (iii), kinetic isotope effects

Scheme I



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[27] (a) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 3641. (b) Lias, S. G. *J. Phys. Chem.* **1984**, *88*, 4401. (b) Freiser, B. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 6893. (c) Martinsen, D. P.; Buttrill, S. E., Jr. *Org. Mass Spectrom.* **1976**, *11*, 762. (d) Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953.

[28] This finding contrasts with the reported extensive H/D scrambling found in the radiolytic isopropylation products from mixtures of perdeuterated benzene (toluene) with unlabeled benzene (toluene): Yamamoto, Y.; Takamuku, S.; Sakurai, H. *J. Am. Chem. Soc.* **1978**, *100*, 2474. However, such extensive H/D exchange referred to experimental conditions, i.e., relatively low pressure of C_3H_8 (100 Torr) and relatively low (1:10) dilution of the aromatic substrates in C_3H_8, which may activate reaction pathways involving excited species, ref 10b.

[29] (a) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034. (b) Koptyug, V. A. In *Contemporary Problems in Carbonium Ion Chemistry III*; Springer Verlag: Berlin, 1984.

[30] Both ions, generated primarily with an arenium structure, undergo unimolecular loss of molecular hydrogen, which, albeit the less unfavorable among unimolecular fragmentations, still requires overcoming an activation barrier exceeding 42 kcal mol^{-1} in the case of $C_7H_9^+$ ions and of 65 kcal mol^{-1} in the case of $C_6H_7^+$ ions. Such values largely exceed the estimated activation energies for 1,2-hydrogen shifts, hence complete scrambling of ring hydrogen atoms was to be expected for $C_6H_7^+$ and $C_7H_9^+$ ions undergoing metastable fragmentations, ref 7.

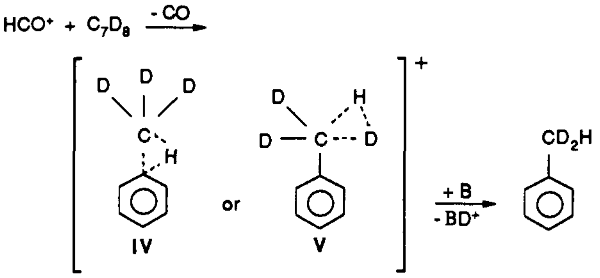
may arise within the framework of Scheme I from the competition of H versus D shifts and from the accompanying changes of hybridization of the H(D)-bearing carbons.

In the absence of added bases, ions I–III may undergo intermolecular proton/deuteron transfer to other toluene molecules or to other bases and proton exchange may also take place. The proton transfer and proton exchange within the collision complexes between toluenium ions and toluene are reportedly slow processes,[27a,31] hence they may be expected to show sizeable primary kinetic isotope effects.[32] However, kinetic isotope effects on the deprotonation of the arenium ions should be suppressed by intervention of a strong base such as acetone, whose PA value, ca. 7 kcal mol^{-1} higher than that of toluene, should ensure fast, indiscriminate proton versus deuteron abstraction from ions I–III. Furthermore it was seen in the alkylation reaction that $(CD_3)_2CO$ was also effective in quenching H/D exchange processes due to proton donor species. Accordingly, we may consider the H distribution in the toluene obtained in the presence of $(CD_3)_2CO$ as representative of the relative abundancies of ions I–III.

Methane Systems. The protonating ability of $CH_5^+/C_2H_5^+$ leads to fairly high yields of H incorporation into the aromatic ring of toluene, slightly favoring the ortho/para positions. Varying amounts of acetone lead to a small but significant shift of the H distribution, favoring the meta at the expense of the para isotopomer at the highest acetone concentration. The observed trend may be viewed as a consequence of the decreased lifetime of the toluenium ions at the higher concentrations of base, which reduces the time allowed to proton shifts. The positional H distributions show a linear dependence on the average lifetime of the toluenium ions (Figure 2). Their intercepts, that reasonably refer to the situation least affected by proton shifts (44% ortho, 37% meta, and 19% para) provide the first evidence on the positional selectivity in the protonation of toluene by the $CH_5^+/C_2H_5^+$ ions. The dependence of the H distribution due to the thermodynamically favored IIa → IIIa isomerization on the ion lifetime leads to a free energy of activation of ca. 8.1 kcal mol^{-1}.[33] It should be noted that the only available value of activation energy for proton shifts within gaseous arenium ions in systems at comparably high pressures, 720–3040 Torr, is close to the present estimate.[33] The positional H distribution measured in the absence of acetone may reflect the contribution of several factors, including H exchange with proton-donor species and differential primary isotope effects for proton vs deuteron removal from ions Ia–IIIa. However, the similarity of H incorporation to alkylation ratios (3.5 ± 0.5) found in the presence and in the absence of added acetone suggests that these effects play a minor role. Furthermore, the occurrence of exchange processes in the collision complexes with H-donor species should lead to double H incorporation in the same toluene molecule, for which no experimental evidence could be found. The latter finding holds also in the presence of C_6H_6 (entry no. 6, Table II), indicating that no H/D exchange between toluenium ions and C_6H_6 takes place, in agreement with previous ICR observations.[31] One additional piece of evidence disproving the occurrence of exchange processes is the observation that the same H distribution is obtained with $CH_5^+/C_2H_5^+$ reactant ions in CH_4 and in H_2/CO with HCO^+ reactant ion, whose Brønsted acidity is intermediate between those of $CH_5^+/C_2H_5^+$ ($PA(CH_4) = 131.6$ kcal mol^{-1}, $PA(C_2H_4) = 162.6$ kcal mol^{-1}, and $PA(CO) = 142$ kcal mol^{-1}). Without added acetone, the nature and the concentration of H-donor species is expected to be widely different in the two systems and so should be their influence on conceivable exchange processes with toluenium ions. The reason why exchange processes may instead occur to a significant extent on alkylated toluenium ions may be traced to their longer lifetime due to the higher PA of their conjugate bases. From the above considerations we are inclined to think that the H incorporation into the ring of the substrate does not suffer from spurious effects but reflects the protonating ability of the reactant ions even in the absence of strong deuterated bases.

Propane Systems. The much lower H incorporation into the substrate noted in the propane systems prevented an analysis of the positional H distribution comparable to that performed in the methane systems. Again, the ratio of H incorporation to alkylation appears to be insensitive to the presence of $(CD_3)_2CO$ (1.5 Torr). The expectation that the milder character as a Brønsted acid of $i\text{-}C_3H_7^+$ should be reflected in a lower abundance of H incorporation into the meta positions, however, was not borne out.

H_2/CO Systems. In the H_2/CO gaseous mixture (entry no. 14, Table II) the reaction of HCO^+ with toluene leads to proton transfer rather than formylation, i.e., no evidence for the formation of tolualdehydes was found, though the addition reaction is estimated to be exothermic by ca. 50 kcal mol^{-1}. The ability of HCO^+ to react efficiently and exclusively with toluene as a Brønsted acid, allowed a specific search at any H incorporation into the methyl group, which could conceivably take place via a phenylmethonium intermediate (eq 4) and provide evidence for its existence. The search yielded negative results, although formation of IV by protonation at the C(methyl)–C(phenyl) bond should be accessible on thermodynamic grounds (cf. $PA(C_2H_6) = 143.6$ kcal mol^{-1}). Clearly, kinetic factors play a major role.



(4)

Proton Transfer versus Alkyl Cation Attachment. Following the arguments outlined in the previous section, we consider the H incorporation into the aromatic substrate as reflecting the protonating ability of the reactant ions, although it will represent only part of the protonation events since a fraction of H will be lost in the deprotonation of the arenium ions. Within these limitation, the H incorporation/alkylation ratios measured in this study are the first data on the branching between protonation and alkylation exhibited by gaseous carbenium ions in the relatively high-pressure range accessible to radiolytic studies.[34] Thus, whereas $i\text{-}C_3H_7^+$ reacts predominantly by cation attachment with the selected arenes, the high H incorporation/alkylation ratios found in the CH_4 systems can only be accounted for by a predominant Brønsted acid behavior of $C_2H_5^+$ ions. In fact, should $C_2H_5^+$ react exclusively as an alkylating agent, the H incorporation/alkylation ratios should be <2.1, i.e., the ratio of CH_5^+ and $C_2H_5^+$ ions formed in the radiolysis of CH_4. The values cluster around 3.5 ± 0.5 in the case of toluene, a ratio unaffected by addition of increasing amounts of $(CD_3)_2CO$. These data lead to a slightly favored alkylation (ca. 70%) rather than protonation (ca. 30%) reactivity by the $C_2H_5^+$ ions. An alternative approach to dissect the relative contribution of the two reaction channels relied on the formation of $C_2D_4H^+$ ions which were let to react with $[^{12}C_6]C_6H_6$. The ensuing $C_6H_5D/C_6H_5C_2D_4H$ yield ratio (entry no. 15, Table II) corresponds to an ca. 50% D-transfer to ca. 50% alkylation branching ratio.[35] A closely similar result,

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[31] Kuck, D.; Ingemann, S.; de Koning, L. J.; Grützmacher, H.-F.; Nibbering, N. M. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 693.

[32] E.g., a kinetic isotope effect $k_H/k_D = 5$ has been derived for the intramolecular proton transfer between phenyl rings in rigid systems: Kuck, D.; Bäther, W.; Grützmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 75.

[33] Rate $= kT/h \exp(-\Delta G^{\ddagger}/RT)$. The value $\Delta G^{\ddagger} = 8.1$ kcal mol^{-1} falls close to $\Delta G^{\ddagger} = 5.2$ kcal mol^{-1} derived from the rate of 1,2 proton shifts within arenium ions bearing isopropyl and trimethylsilyl substituents: Attinà, M.; Cacace, F.; Ricci, A. *J. Am. Chem. Soc.* **1991**, *113*, 5937.

[34] Tritium-labeled isopropyl cations have successfully been used to demonstrate their protonating reactivity toward thiophene, under radiolytic conditions. However, no estimates on the branching ratio between the protonation and alkylation channel have been given: Bucci, R.; Laguzzi, G. *Radiochim. Acta* **1990**, *51*, 177.

46% H-transfer vs 54% alkylation, can be derived from entry no. 1, Table II, where the $C_6D_5H/C_6D_5C_2H_5$ yield ratio of 5 was obtained from the reaction of $CH_5^+/C_2H_5^+$ with C_6D_6.

The H incorporation/alkylation ratios obtained in methane show no correlation with the increasing basicities of the arenes: benzene < toluene < *o*-xylene, probably due to the fact that proton transfer from $C_2H_5^+$ ions to all members of the series is highly exothermic and the exothermicities of cation attachment are even higher, as reported in Table III.

i-$C_3H_7^+$ ions look much less prone to react as Brønsted acids. Their nearly thermoneutral proton transfer to benzene leads to a negligible degree of H incorporation by this substrate, but even the exothermic proton transfer to toluene is much less efficient (ca. 8%) than the alkylation channel (ca. 92%). The former can somewhat be enhanced (ca. 18%) by increasing the temperature or decreasing the pressure of propane, i.e., on approaching conditions closer to those prevailing in CI mass spectrometry. The H incorporation/alkylation ratio is not affected by acetone, as observed in the CH_4 systems. Thus, also in the case of *i*-$C_3H_7^+$ ions, the branching ratio between the protonation and the alkylation routes is unaffected by the base, hence by the decreased arenium ion lifetime. Such seemingly inherently constant ratio is hardly compatible with an addition–elimination mechanism. In fact, both the lower exothermicity of the *i*-$C_3H_7^+$ vs $C_2H_5^+$ cation attachment and the increased number of degrees of freedom in the arenium ion formed should depress its dissociation rate and bring the process to a time scale comparable to the frequencies of collisions with the moderating bath propane gas as well as with the added base. This observation would suggest the existence of an intrinsic branching ratio between the protonation and alkylation route and that the two competitive channels do not share the same intermediate.

Conclusions

The gas-phase reaction of cationic electrophiles with arenes presents multifaceted aspects, some of which have so far escaped attention, despite the many studies concerning this important class of reactions. Among them, the sites of kinetic attack by the proton, the simplest among all electrophiles, in the reactions of gaseous arenes with Brønsted acids could never be assessed by mass spectrometric techniques. The use of the radiolytic technique, operating at higher pressures, coupled to NMR analysis of the neutral radiolytic products of ion–molecule reactions, a relatively novel expansion of the capabilities of the radiolytic technique, has allowed to address this problem. In particular, this study on perdeuterated arenes has provided previously unaccessible information on the following features: (i) the kinetic sites of protonation by the $CH_5^+/C_2H_5^+$ ions on toluene (44% ortho, 37% meta, and 19% para); (ii) the free energy of activation for the meta → para hydrogen shift in toluenium ions, ca. 8.1 kcal mol^{-1}, a value comparable to that for hydrogen shift in benzenium ions in superacid solutions; (iii) the significant Brønsted acid reactivity of $C_2H_5^+$ ions toward simple arenes at the relatively high pressures prevailing in the radiolytic systems, in contrast with the predominant alkylating ability of $C_3H_7^+$ ions. The dual behavior of ethyl cations toward benzene has been checked by two complementary approaches, the reaction of $C_2H_5^+$ ions (in the 2.1:1 $CH_5^+/C_2H_5^+$ mixture from the radiolysis of methane) with C_6D_6 and the reaction of $C_2D_4H^+$ ions (from the protonation of C_2D_4 by $CH_5^+/C_2H_5^+$) with $[^{12}C_6]C_6H_6$, both yielding a comparable extent of H(D) transfer vs alkylation. Whereas no generalizations can be made of results concerning only two cations, ethyl and isopropyl, it is apparent that higher reaction exothermicity favors the protonation channel. This may result from an intrinsic trend in relative activation energies for carbon and proton attachment or from a fast addition–elimination pathway which is not suppressed even under relatively high-pressure conditions (i.e., within $\approx 10^{-10}$ s). Our interpretation of the experimental data suggests that protonation and alkylation proceed indeed by two distinct pathways, though a conclusive proof requires further investigation.

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Registry No. Ethyl cation, 14936-94-8; isopropyl cation, 19252-53-0; formyl cation, 17030-74-9; benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6.

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(35) We have assumed that $C_2D_4H^+$ ions have undergone complete H/D scrambling prior to reaction with benzene as it is suggested by the statistical distribution of H/D atoms in the ethyl group of C_6H_5–C_2D_4H, in agreement with previous gas- and liquid-phase data. According to recent ab initio calculations, ethyl cations exist in a bridged structure; however, the H/D scrambling noted above would indicate that $C_2D_4H^+$ ions from the protonation of ethylene-*d*$_4$ by the $CH_5^+/C_2H_5^+$ ions do not retain the proton in the bridged position, rather they undergo statistical H/D mixing. (a) Wong, M. W.; Baker, J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2245. (b) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (c) Hirao, K.; Yamabe, S. *Chem. Phys.* **1984**, *89*, 237. (d) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067. (e) Vorachek, J. H.; Meisels, G. G.; Geanangel, R. A.; Emmel, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 4078.