formation provided by single crystal/UHV studies can be used to improve the design and processing of CVD precursors.

4. Experimental Section

High-resolution EELS, TPD, and IDMS experiments were performed in a diffusion- and titanium-sublimation-pumped ultra-high-vacuum chamber with a base pressure near 1×10^{-10} Torr. The system was equipped with four-grid low-energy electron diffraction (LEED) optics (Varian), a single-pass cylindrical mirror analyzer (PHI) for Auger electron spectroscopy (AES), a differentially pumped quadrupole mass spectrometer (Vacuum Generators), and a high-resolution electron energy loss spectrometer (McAllister Technical Services). For the EELS experiments, the angle of the incident electron beam (60° to the surface normal) and its energy (4–5 eV) were held constant and electrons were collected only in the specular direction. The elastic scattering peak from an adsorbate-covered surface had an intensity of $>10^5$ cps and a full width at half maximum of 6–8 meV (50–60 cm^{-1}). For the TPD and IDMS experiments the heating rate was 2 K/s.

Infrared experiments were conducted in a second small UHV chamber also equipped for Auger electron spectroscopy and low-energy electron diffraction. The system was interfaced to a conventional Fourier transform infrared spectrometer (Mattson Instruments) using reflection optics ($\sim f/15$). The angle of incidence was 85° and only the reflected, p-polarized light was collected using a liquid nitrogen cooled, narrow band MCT detector. Typically 2048 scans were averaged at 4-cm^{-1} resolution. In the variable temperature experiments, the sample was raised to the indicated temperature for ~2 s and then cooled to the dosing temperature before data collection was initiated.

The 1–1.3-cm diameter Cu(111) and Cu(100) single crystal disks (>99.999%, Monocrystals) were oriented, cut, and polished using standard techniques. The samples were mounted on small, temperature-controlled molybdenum blocks which could be heated to ~1200 K by a tungsten filament or cooled to ~100 K via copper braids attached to a liquid nitrogen reservoir. Temperatures were measured using a chromel–alumel thermocouple inserted into the copper substrate. The crystals were cleaned of trace carbon, sulfur, and oxygen impurities by repeating cycles of neon ion sputtering (1000 eV, 8–10 $\mu A/cm^2$) at both 300 and 970 K followed by annealing in vacuum at 970 K. Sample cleanliness and order were carefully monitored by AES and LEED, respectively. Samples were sputtered and annealed before each adsorption experiment.

Anhydrous $Cu(hfac)_2$ and hfacH (99%) were purchased from Strem. Cu(hfac)(vtms) was obtained from Schumacher. $Cu(acac)_2$ (97%), acacH (99+%), and vtms (97%) were purchased from Aldrich. All adsorbates were thoroughly degassed by repeated freeze–pump–thaw cycles prior to introduction into the vacuum chambers. Care was taken to completely dehydrate the $Cu(hfac)_2$ (dark purple crystals) by heating under vacuum prior to dosing. Gas dosing of the more volatile species was performed by backfilling the UHV systems while the lower vapor pressure materials were introduced into the chambers through a heated, effusive molecular beam doser. Further, the headgas from the Cu(hfac)(vtms) source was continuously pumped during dosing in order to minimize vtms contamination in the effluent. Gas exposures were not corrected for the varying sensitivities of the different ionization gauges.

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Interannular Proton Transfer in Thermal Arenium Ions from the Gas-Phase Alkylation of 1,2-Diphenylethane

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Abstract: The first demonstration of *thermal* interannular proton shifts in gaseous bicyclic arenium ions and the evaluation of their Arrhenius parameters have been achieved with the radiolytic technique. The model ions have been obtained by alkylation of $C_6D_5CH_2CH_2C_6H_5$ with radiolytically formed Me_3C^+ ions in isobutane at sufficiently high pressure (630–1730 Torr) to ensure that the processes of interest obey thermal kinetics. From the extent of interannular H/D scrambling in the alkylated products, measured as a function of the arenium ions' lifetime, the rate constant for the $H^+(D^+)$ ring-to-ring transfer in the para-substituted arenium ions has been estimated to be $(1.3 \pm 0.4) \times 10^7$ $((2.9 \pm 0.6) \times 10^6)$ s^{-1} at 47 °C. A temperature-dependence study covering the range from 47 to 150 °C has allowed the evaluation of the Arrhenius parameters for the interannular $H^+(D^+)$ transfer, giving $E_a = 6.3 \pm 0.2$ (8.0 ± 0.2) kcal mol^{-1} and $\log A = 11.4 \pm 0.4$ (11.9 ± 0.3). Further mechanistic insight into the detailed mechanism of gas-phase alkylation is provided by other kinetic results. In particular, the significant interannular H/D discrimination of Me_3C^+, which favors the unlabeled ring of $C_6D_5CH_2CH_2C_6H_5$ by a factor of 1.7 at 47 °C, provides further evidence for the reversible character of aromatic *tert*-butylation suggested by previous radiolytic and mass spectrometric studies on monocyclic arenes. The higher *tert*-butylation rate (2.9:1 at 120 °C) of 1,2-diphenylethane than of toluene supports recent mass spectrometric results pointing to the formation of stable complexes between Me_3C^+ and α,ω-diphenylalkanes.

Proton shifts in aromatic systems have been the subject of extensive studies by NMR techniques in acid solutions[1] and by computational methods.[2] Their occurrence in gaseous arenium ions is well documented by the results of chemical ionization (CI) and ion cyclotron resonance (ICR) mass spectrometric investigations.[3] A kinetic study was recently reported of 1,2 proton shifts in gaseous arenium ions[4] based on the radiolytic technique,[5] which

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Table I. Gas-Phase Reaction of Me_3C^+ with $C_6H_5(CH_2)_2\text{–}C_6D_5$

system composition (Torr)[a]				products: *m*- and *p-tert*-butyldiphenylethane													
				isomeric[b] composition (%)		isotopic composition[b]											
1,2-diphenylethane	triethylamine	$i\text{-}C_4H_{10}$	t, °C			$\frac{Me_3C\text{–}C_{14}H_8D_5}{Me_3C\text{–}C_{14}H_9D_4}$		$\frac{Me_3C_6H_4\text{–}CH_2^+}{Me_3C\text{–}C_6H_3D\text{–}CH_2^+}$		$\frac{Me_3C_6D_4\text{–}CH_2^+}{Me_3C_6HD_3\text{–}CH_2^+}$		$\frac{C_6H_5\text{–}CH_2^+}{C_6H_4D\text{–}CH_2^+}$		$\frac{C_6D_5\text{–}CH_2^+}{C_6HD_4\text{–}CH_2^+}$			
				meta	para	meta	para	meta	para	meta	para	meta	para	meta	para		
0.35		690	47	44	56	1.68	1.44	25.4	50.8	6.1	10.6	11.0	10.0	4.2	4.8		
0.35	0.51	690	47	44	56	1.52	1.30	27.0	56.3	9.2	13.6		14.0	4.7	5.8		
0.54	0.13	630	90	54	46	1.65	1.80	19.4	6.3	7.9	4.3	7.0	4.4	3.0	2.7		
0.78	0.34	650	90	53	47	1.57	1.73	18.4	7.7	7.5	4.4	6.9	5.1	3.1	2.9		
0.61	0.47	640	90	53	47	1.65	1.72	21.2	11.1	12.1	5.6	7.6	6.4	3.0	3.3		
0.61		700	120	63	37	1.60	1.65	8.0	2.1	3.0	1.9	4.3	1.9	2.5	1.3		
0.49[c]	0.36	630	120	66	44	1.37	1.40	11.6	3.4	5.3	2.8	5.3	2.7	2.8	2.1		
0.58	0.45	660	120	60	40	1.45	1.58	11.7	3.1	6.3	2.8	5.5	2.7	2.6	1.8		
0.70	0.78	650	120	61	39	1.48	1.58	14.4	3.8	7.8	3.3	7.1	3.3	2.8	1.9		
0.63	1.46	650	120	57	43	1.45	1.58	19.8	6.5	11.3	5.6	7.8	4.7	3.0	2.6		
0.79	4.34	640	120	50	50	1.48	1.57	26.0	18.7	14.4	9.6	8.2	7.5	3.1	3.7		
0.98	1.78	1730	120	48	52	1.25	1.38	19.7	29.0	20.6	16.0	5.4	9.4	3.4	3.9		
0.95	0.46	640	150	66	34	1.50	1.56	9.4	2.5	5.0	2.1	4.6	2.2	2.3	1.4		
0.76	1.19	640	150	63	37	1.48	1.54	14.1	3.6	7.5	3.3	5.9	3.0	2.6	1.7		
0.72	2.45	640	150	60	40	1.48	1.56	18.3	6.7	10.5	5.2	7.4	4.5	2.9	2.5		

[a] All gaseous systems contained O_2 (10 Torr) as a radical scavenger. [b] Standard deviation ±10%. [c] The system contained, in addition, toluene (0.66 Torr). The competition gave a $k_{(DPE)}/k_{(C_7H_8)}$ ratio of 2.9 ± 0.3.

differs from mass spectrometric approaches in two important respects. In the first place, the ions are radiolytically formed in a bath gas at sufficiently high pressure (760 Torr and above) to ensure their collisional thermalization *before* proton shifts can occur. Under such conditions, hardly accessible to mass spectrometric methods, a realistic definition of the reaction temperature becomes possible and the reaction obeys thermal kinetics, displaying a regular, *positive* temperature dependence. In the second place, the time resolution allowed by the radiolytic technique, of the order of nanoseconds, far exceeds that typical of mass spectrometric approaches, allowing the kinetic study of fast processes, such as proton shifts in arenium ions. The unique features of the radiolytic technique, complemented by isotopic labeling and temperature-dependence experiments, have allowed the derivation of Arrhenius parameters of 1,2 proton shifts in substituted benzenium ions and the measurement of the H/D kinetic isotope effect (KIE) of these processes.[4]

We report here on the extension of the study to a different type of intramolecular proton shift, namely, ring-to-ring proton migration in (β-phenylethyl)arenium ions from the cationic alkylation of 1,2-diphenylethane (DPE), the most simple α,ω-diphenylalkane whose protonated adduct has been shown by mass spectrometric techniques to undergo extensive interannular hydrogen migration.[3,6,7] Indeed, complete equilibration of all 11 aromatic hydrogen atoms occurs before fragmentation in those (2-phenylethyl)benzenium ions that are sufficiently excited to undergo metastable loss of benzene in the 10-μs time frame of the mass spectrometric experiments.[6,7] The charged alkylating agent used in this work, Me_3C^+, is a mild electrophile whose gas-phase reactions with the arenes, in particular benzene and toluene, have been thoroughly investigated both from the thermochemical and from the kinetic standpoint with mass spectrometric and radiolytic techniques.[8-13] In particular, the reaction of Me_3C^+ with selectively deuterated toluenes has been used to obtain the gaseous arenium ions whose 1,2 proton shifts have been studied with the radiolytic technique,[4] whereas its reactions with simple alkylbenzenes and α,ω-diphenylalkanes have recently been investigated with mass spectrometric techniques to probe the formation of ion–neutral complexes.[14]

The experimental approach followed in the present study can be outlined as follows: Me_3C^+ ions from the radiolysis of $i\text{-}C_4H_{10}$ are allowed to react with $C_6H_5CH_2CH_2C_6D_5$ in isobutane gas at pressures ranging from 630 to 1730 Torr. The arenium ions from the cationic alkylation are eventually deprotonated by Et_3N, yielding as the end product a mixture of isomeric (2-phenylethyl)-*tert*-butylbenzenes whose yields, isomeric composition, and intramolecular D distribution are determined by GC MS. The lifetime of the arenium ions and hence the time allowed for the occurrence of intramolecular proton shifts before quenching by Et_3N depend on the concentration of the latter, which has been varied over a 30-fold range. The temperature dependence of the rate of proton shifts has been investigated by performing the radiolytic alkylation at temperatures ranging from 47 to 150 °C.

Experimental Section

Materials. $i\text{-}C_4H_{10}$, CH_4, and O_2 were research-grade gases from Matheson Co. with a stated purity exceeding 99.98 mol %. Most other chemicals used, including toluene and 1,2-diphenylethane, were obtained from commercial sources. $C_6H_5CH_2CH_2C_6D_5$ was obtained as described in ref 7 and purified by recrystallization from cold ethanol.

Procedure. The gaseous samples were prepared using standard vacuum procedures in sealed 135-mL Pyrex vessels according to the techniques previously illustrated in detail.[4] The competition experiments between toluene and DPE required a long equilibration time (>5 h at 130 °C) in order to allow for complete vaporization of the less volatile substrate. The irradiations were performed in a 220 Gammacell (Nuclear Canada Ltd.) at total doses ranging from 1×10^4 to 2×10^4 Gy at a dose rate of 2×10^4 Gy h^{-1}. The radiolytic products were extracted by freezing the vessels at 77 K and then washing their inner walls with ethyl acetate with repeated freeze–thaw cycles. The products were separated and their D content analyzed by GC MS using the following columns mounted in a Hewlett-Packard 5890A gas chromatograph equipped with a Model 5970B mass-selective detector or in a Perkin-Elmer Model 8700 gas chromatograph equipped with a standard FID detector: (i) a 50-m long, 0.2-mm i.d. fused silica column coated with a 0.5-μm cross-linked

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methylsilicone film (PONA column from Hewlett-Packard Co.) operated isothermally (2 min) at 65 °C and then heated at the rate of 5 deg min^{-1} to 130 °C and subsequently at 16 deg min^{-1} to 230 °C; (ii) a 60-m long, 0.25-mm i.d. fused silica column coated with a 0.25-μm film of 20% diphenyl-, 80% dimethylpolysiloxane (SPB-20 column from Supelco Co.), operated at 100 °C (5 min) and then heated at the rate of 10 deg min^{-1} to 120 °C and at 15 deg min^{-1} to 230 °C.

Results

The composition of the irradiated systems, the products formed, their total D content, and the D distribution in the two rings are reported in Table I. As in analogous radiolytic studies, the ionic character of the alkylation is ensured by a large excess (10 Torr) of O_2, an effective radical scavenger, and is independently confirmed by the depression of the yields caused by the presence of a gaseous base (Et_3N) which efficiently intercepts the Me_3C^+ ions. Thus, the combined yields of the *tert*-butylated products drop from a G value of 1.1 molecules/100 eV in the absence of added bases to the values of 0.53, 0.39, and 0.29, measured in the presence of 0.78, 1.46, and 2.61 Torr of Et_3N, respectively.

The approach followed to evaluate the content and the distribution of D in the products and the way the results are reported in Table I deserve a brief explanation. The 70-eV EI mass spectra of unlabeled *tert*-butyldiphenylethanes display as the base peak (100%) the $Me_3C–C_7H_6^+$ *tert*-butylated benzyl ion, m/z = 147, together with the molecular ion at m/z = 238 (ca. 40%) and the $C_7H_7^+$ unsubstituted benzyl ion at m/z = 91 (ca. 30%). The molecular ions of the deuterated *tert*-butyldiphenylethanes from the alkylation of $C_6D_5CH_2CH_2C_6H_5$ consist of two isotopomers at m/z = 243 and 242, whose ratio reflects the relative extent of H versus D displacement in the electrophilic aromatic substitution by Me_3C^+ ions. This ratio, reported in Table I, allows one to estimate the relative rate of alkylation of the unlabeled and of the fully deuterated ring, under the assumption that only H^+ is lost in the former case and D^+ in the latter, which is an acceptable approximation in view of the observed extent of H/D interannular migration (vide infra). The 70-eV EI mass spectrum of $C_6D_5CH_2CH_2C_6H_5$ displays equal abundances of $C_6D_5CH_2^+$ and $C_6H_5CH_2^+$ ions without detectable amounts of isotopically mixed fragments, such as $C_6HD_4CH_2^+$, $C_6H_2D_3CH_2^+$, etc., indicative of interannular H/D scrambling induced by the ionization process. Such a feature sets DPE apart from the higher α,ω-diphenylalkanes,[15] where EI ionization promotes extensive H/D mixing in the benzyl fragment ions, and allows GC MS to be used for evaluating the intramolecular D distribution in the alkylated products from the radiolysis. Their mass spectra display a family of peaks at m/z values ranging from 147 to 151, assigned to $Me_3C–C_6X_4–CH_2^+$ (X = H, D) ions containing 0–4 D atoms, and a family of peaks at m/z values ranging from 91 to 96, assigned to $C_6X_5CH_2^+$ ions containing 0–5 D atoms.

In the first family the most abundant isotopomers are the "unscrambled" $Me_3C–C_6H_4–CH_2^+$ and $Me_3C–C_6D_4–CH_2^+$ ions, i.e., those containing only aromatic hydrogen atoms of the original isotopic composition, unmixed with the hydrogen atoms of the other ring, henceforth denoted as ions of type A. In addition, there are significant peaks of the $Me_3C–C_6H_3D–CH_2^+$ and $Me_3C–C_6HD_3–CH_2^+$ isotopomers, i.e. "singly exchanged" ions which contain one hydrogen atom from the other ring, henceforth denoted as ions of type B. The abundances of the latter ions are higher from the alkylated products obtained at higher temperatures and/or at lower Et_3N concentrations. Analogous trends characterize the family of $C_6X_5CH_2^+$ ions, where the type-A ions $C_6D_5CH_2^+$ and $C_6H_5CH_2^+$ predominate and the abundances of the type-B ions C_6HD_4-CH_2^+ and $C_6H_4D–CH_2^+$ also increase when the alkylation is carried out at higher temperatures and/or at lower Et_3N concentrations. We shall neglect in this discussion the fragments characterized by a more extensive H/D exchange, e.g., the $Me_3C–C_6H_2D_2–CH_2^+$ and $C_6H_2D_3CH_2^+$ ions, since their abundances are, in general, significantly lower than those of ions B and, in addition, show no well-defined dependence on the temperature and on the concentration of Et_3N.

On the basis of the above considerations, the ratios of the abundances of ions of types A and B in each family of $Me_3C–C_6X_4–CH_2^+$ and of $C_6X_5CH_2^+$ isotopomers, which are related to the extent of H/D interannular exchange in the alkylated products obtained under different experimental conditions, are reported in the last entries of Table I.

Interannular Isotopic Discrimination and Positional Selectivity. From the data of Table I it is apparent that the alkylation rate of the $C_6D_5CH_2CH_2C_6H_5$ rings is different, being higher for the unlabeled ring under all reaction conditions examined. The ratio of alkylation on the C_6H_5 compared to the C_6D_5 moieties reaches its highest value, 1.7, at the lowest temperature, 47 °C, in the absence of added bases and decreases at higher temperatures and/or in the presence of increasing concentrations of Et_3N, within the scatter of the data.

The positional selectivity is also appreciably affected by the temperature and by the concentration of the base. Taking into account reactions carried out in the presence of a nearly constant concentration (0.57–0.62 Torr) of Et_3N, the para:$^1/_2$-meta ratio is found to decrease regularly from 2.54 at 47 °C to 1.77 at 90 °C, 1.33 at 120 °C, down to 1.06 at 150 °C. At any given temperature, increasing [Et_3N] leads to a significant enhancement of para substitution, e.g., at 120 °C the para:$^1/_2$-meta ratio increases from 1.17 in the absence of added bases to 2.00 in the presence of 5.72 Torr of Et_3N. Finally, the results of competition experiments show that DPE undergoes *tert*-butylation faster than toluene, e.g., the ratio of the rate constants is 2.9 ± 0.3 at 120 °C.

Interannular H^+ and D^+ Transfers. Direct information on the H^+ and D^+ migration from the *tert*-butylated ring to the unsubstituted ("spectator") ring of DPE is provided by the $C_6D_5CH_2^+/C_6HD_4CH_2^+$ and by the $C_6H_5CH_2^+/C_6H_4DCH_2^+$ abundance ratios in the EI mass spectra of the alkylated products. Whereas the quantitative treatment of the data is deferred to a following section, it is apparent that the higher the rate of the H^+ and the D^+ ring-to-ring transfers, the lower the $C_6D_5CH_2^+/C_6HD_4CH_2^+$ and the $C_6H_5CH_2^+/C_6H_4DCH_2^+$ ratio, respectively. The rate of H^+ migration to the spectator ring is found to invariably exceed that of D^+ migration. A mechanistically informative feature is that the extent of $H^+(D^+)$ interannular transfers is generally higher in the para- than in the meta-substituted products from the same reaction and increases at higher temperatures and/or at lower concentrations of Et_3N. In the EI mass spectra of the *tert*-butylated products, the detection of $Me_3C–C_6HD_3–CH_2^+$ and of $Me_3C–C_6H_3D–CH_2^+$ ions, in addition to the isotopically intact $Me_3C–CD_4–CH_3^+$ and $Me_3C–C_6D_4–CH_2^+$ fragments, indicates the occurrence of consecutive $H^+(D^+)$ transfers from, and subsequently back to, the substituted ring. This view is consistent, inter alia, with the fact that the $Me_3C–C_6D_4–CH_2^+/Me_3C–C_6HD_3–CH_2^+$ and the $Me_3C–C_6H_4–CH_2^+/Me_3C–C_6H_3D–CH_2^+$ ratios show a more pronounced dependence on [Et_3N] than the corresponding $C_6D_5CH_2^+/C_6HD_4CH_2^+$ and $C_6H_5CH_2^+/C_6H_4DCH_2^+$ ratios.

Discussion

General Mechanistic Features of Gas-Phase Aromatic *tert*-Butylation. Gaseous Me_3C^+ is a relatively mild electrophile whose formation in the γ-radiolysis of neopentane or isobutane at atmospheric pressure and whose reactivity toward model aromatic substrates are well documented.[4,5,8-13] The general mechanistic picture of the gas-phase aromatic alkylation by thermal Me_3C^+ ions, delineated by extensive mass spectrometric and radiolytic studies, is illustrated in Scheme I.

The first step of the alkylation is the formation of a collision complex, stabilized by the electrostatic interaction of the cation with the aromatic substrate, in particular with its π-electrons, and hence legitimately regarded as the gas-phase counterpart of the π-complexes postulated in solution. Complex **1**, thermalized by unreactive collisions in the dense bath gas,[16] undergoes reversible

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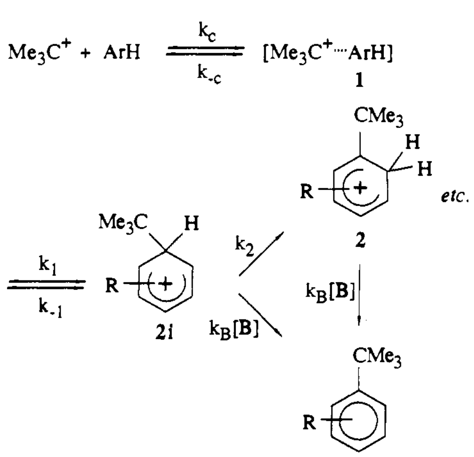
(16) In a dense gas at pressures ≥1 atm the ion–molecule collision frequency is of the order of ≥ 10^{11} s^{-1}.

Scheme I

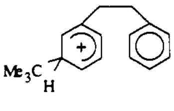


conversion into an ipso-substituted arenium ion (**2i**) (σ-complex) whose fate depends on the competition between back-dissociation and those processes, i.e., intramolecular proton shifts or deprotonation by a gaseous base B, which tend to remove the proton from the ipso carbon, making alkylation irreversible. Scheme I can be extended to diphenylalkanes, such as DPE (R = CH_2CH_2Ph), by taking into account two distinctive features of the latter. First, in addition to intraannular proton shifts,[3,17] interannular shifts are possible in the (phenylalkyl)arenium ions formed by electrophilic alkylation. Second, the spectator ring stabilizes both intermediates **1** and **2** from α,ω-diphenylalkanes with respect to the corresponding species from single ring substrates. Since the Me_3C^+ cation is "disolvated" by the two aromatic rings in the $[Me_3C^+\cdots C_6H_5CH_2CH_2C_6H_5]$ complex, the binding energy of the latter is expected to be higher than that of the $[Me_3C^+\cdots C_6H_5CH_3]$ complex, estimated to be 12 kcal mol^{-1}.[18,19] A stabilizing effect is also expected in (β-phenylethyl)arenium ions **2**, where the arenium ion formed upon alkylation can be viewed as "solvated" by the spectator ring. The stabilizing effect of a benzene ring solvating a gaseous arenium ion can be estimated in several ways. An upper limit is probably the binding energy of the $[C_6H_7^+\cdots C_6H_6]$ complex, as high as 11 kcal mol^{-1}.[18] A more realistic value for the system of interest can be derived by comparing the proton affinity (PA) of toluene, 189.8 kcal mol^{-1}, and of DPE, 194.6 kcal mol^{-1}.[20] The difference, 4.8 kcal mol^{-1}, can hardly reflect different activating effects of the Me and the $PhCH_2CH_2$ substituents, whose electron-releasing ability is certainly comparable, as witnessed by their very close σ and σ^+ constants.[21] The difference is likely to arise from the stabilizing effect of the spectator ring of DPE, which consequently can be estimated to be around 5 kcal mol^{-1}. Hence, the overall exothermicity of the alkylation

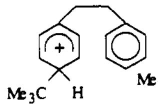
$$Me_3C^+ + C_6H_5CH_2CH_2C_6H_5 \rightarrow C_6H_5CH_2CH_2C_6H_5CMe_3^+$$

is likely to exceed by $\approx$5 kcal mol^{-1} that of the *tert*-butylation of toluene, 29.1 ± 0.3 kcal mol^{-1},[9] both values referring to the formation of the most stable arenium ion.

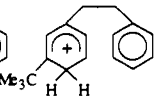
Energetics of Interannular Proton Shifts. Before discussing the kinetic aspects of the interannular proton shifts in the arenium ions from DPE, it is useful to consider their energetics. The available theoretical and experimental evidence suggests that alkyl groups such as Me and Me_3C increase appreciably (6–12 kcal mol^{-1}) the PA of the ortho and para positions with respect to that of C_6H_6, whereas the ipso and the meta positions are little affected.[22,23] As in the case of toluene, the steric requirements of Me_3C^+ allow alkylation exclusively at the meta and para positions of DPE, yielding the corresponding ipso-substituted ions **2i**(*m*), **2i**(*p*), **2**(*m*), and **2**(*p*).



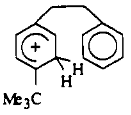
2i(m)



2i(p)



2(m)



2(p)

An important factor which controls the rate of interannular proton transfer to the spectator ring is the difference between the local PAs of the positions involved. It should be noted that the H^+ transfer to the spectator ring does not necessarily occur from the ipso-alkylated carbon, owing to the occurrence of fast *intraannular* H^+ shifts that convert **2i**(*m*) and **2i**(*p*) into more stable protomers.[3] On the basis of the rate of 1,2 $H^+(D^+)$ shift in *m-tert*-butyltoluenium ions,[4] **2i**(*m*) is expected to undergo very fast intraannular proton shifts to those positions (2, 4, and 6) which are activated by two ortho/para alkyl groups. Subsequent H^+ migration to the spectator ring is hampered by the lower basicity of the latter, whose positions are activated at most by a single alkyl group, which would make interannular transfer endothermic by some 6 kcal mol^{-1}.[22] The situation is different in the para-alkylated arenium ions, where all ring positions are activated by only one ortho/para and one meta alkyl group. Intraannular H^+ shifts would convert **2i**(*p*) into protomers, such as **2**(*p*), still capable of undergoing a nearly thermoneutral H^+ transfer to the most basic positions of the spectator ring.

The above considerations provide a neat explanation for the considerably more extensive H/D scrambling observed in the para- than in the meta-alkylated products.

In this context, it may be recalled that previous mass spectrometric studies did not show any effect of methyl or methoxy substituents on the rate of the interannular proton exchange.[24] Only for PA differences above ca. 36 kcal mol^{-1} of the arene rings was a suppression of this process found.[24a]

Kinetics of Interannular Proton Shifts. Whereas the H/D exchange observed in the *tert*-butylated products from $C_6D_5CH_2CH_2C_6H_5$ demonstrates the occurrence of ring-to-ring $H^+(D^+)$ transfers, working out a kinetic model which accomodates all such processes is difficult. The complexity of the reaction sequences promoted by the Me_3C^+ attack, which can occur either on the unlabeled or on the deuterated ring and which gives in both cases either a meta- or a para-substituted arenium ion via a reversible addition process followed by $H^+(D^+)$ intraannular and interannular shifts, is reflected even in the partial and simplified outline given in Scheme II, which refers to para substitution of the deuterated ring (a similar scheme can be written for para substitution of the unlabeled ring). In view of the great difficulty of a comprehensive kinetic analysis, we have focused attention on a single representative process, namely, the first $H^+(D^+)$ shift from the alkylated ring of intermediate **2** to the most basic positions (2, 4, and 6) of the spectator ring. This particular interannular proton transfer has been chosen for being the one which occurs to the largest extent and is the best defined regarding the reaction centers involved (vide infra). The rate constants of the H^+ and D^+ transfers taken into account (e.g., $k_{2(D)}$ in Scheme II) have been estimated by adopting the following approximations: (i) deprotonation of the arenium ions by Et_3N occurs with 100% collision efficiency and without H/D isotopic discrimination and (ii) the rate of the subsequent interannular shifts, i.e., those yielding ions **4**, **5**, etc. (Scheme II), is comparatively low, which allows such processes to be neglected in the evaluation of $k_{2(H)}$ and $k_{2(D)}$.

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(17) Kuck, D.; Bäther, W. *Org. Mass Spectrom.* **1986**, *21*, 451.

(18) Mautner, M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 5466.

(19) Estimated in ref 4 on the basis of the binding energy of the $[Me_2Cl^+\cdots C_6H_5CH_3]$ complex reported by Sharma, D. K. S.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19.

(20) 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*.

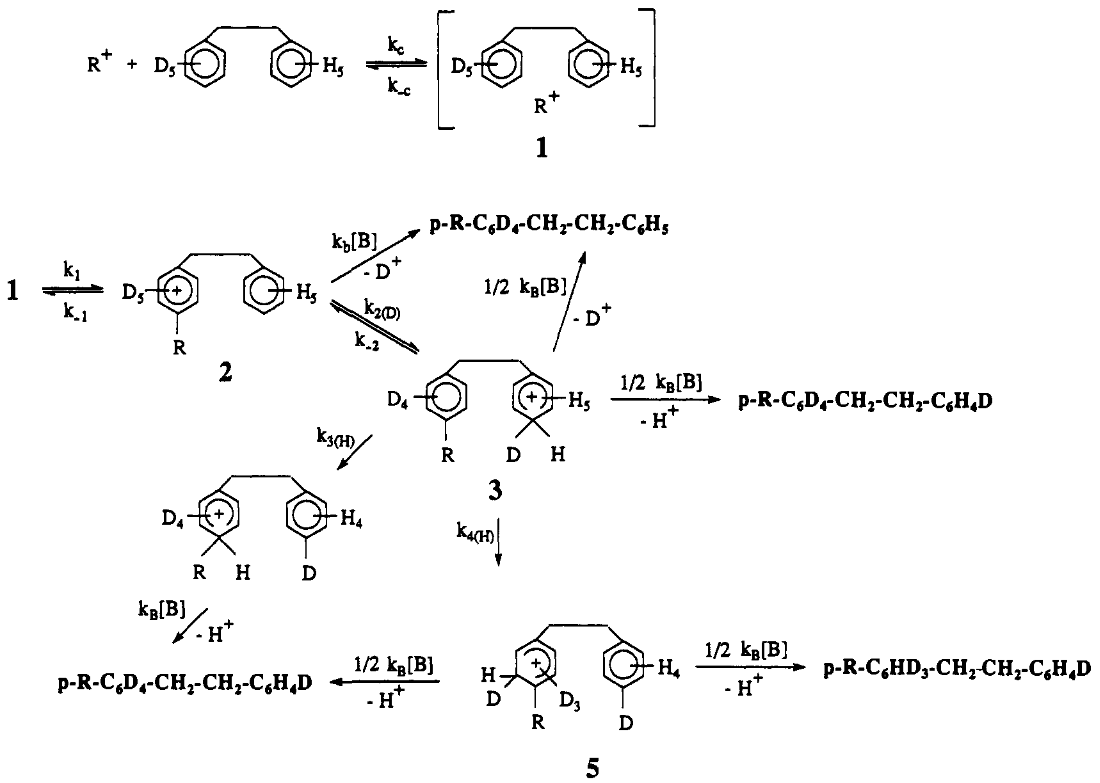
(21) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, **1990**.

(22) Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 1990.

(23) Cacace, F.; Crestoni, M. E.; de Petris, G.; Fornarini, S.; Grandinetti, F. *Can. J. Chem.* **1988**, *66*, 3099.

(24) (a) Bäther, W.; Kuck, D.; Grützmacher, H.-F. *Org. Mass Spectrom.* **1985**, *20*, 589. (b) Kuck, D., unpublished results.

Scheme II



The first approximation is reasonable, since exothermic proton-transfer reactions to *n*-type bases, unless sterically hindered, are generally very fast in the gas phase. Furthermore, there is a large basicity difference between the *tert*-butylated arenes (PA < 201 kcal mol^{-1}) and Et_3N (PA = 232.3 kcal mol^{-1}),[20] which corresponds to a sufficiently large pK_a difference to place the deprotonation well outside the region around $\Delta pK_a = 0$, where the maximum H/D kinetic isotope effect (KIE) can occur according to the Bell criterion.[25]

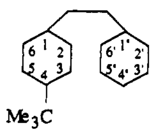
The second approximation appears at first sight rather crude, especially since the H/D exchange observed in the alkylated ring of the products provides direct evidence for the occurrence of shifts yielding ions **4**, **5**, etc. However, as these secondary processes occur in most cases to an extent significantly lower than the initial $H^+(D^+)$ shift from the alkylated to the spectator ring, their neglect does not cause intolerably large errors, introducing an uncertainty estimated to be <30% into the calculated values of the $k_{2(H)}$ and $k_{2(D)}$ rate constants.

Using the above approximations, a conventional steady-state treatment predicts a linear dependence on the base concentration of the ratios of the yields of "unexchanged" to "singly exchanged" products and hence of the abundances of the corresponding benzyl ions in their EI mass spectra:

$$\frac{[Me_3C\text{–}C_6H_4CH_2CH_2C_6D_5]}{[Me_3C\text{–}C_6H_4CH_2CH_2C_6HD_4]} = \frac{[C_6D_5CH_2{}^+]}{C_6HD_4CH_2{}^+} = \frac{2k_B[B]}{k_{2(H)}}$$

$$\frac{[Me_3C\text{–}C_6D_4CH_2CH_2C_6H_5]}{[Me_3C\text{–}C_6D_4CH_2CH_2C_6H_4D]} = \frac{[C_6H_5CH_2{}^+]}{[C_6H_4DCH_2{}^+]} = \frac{2k_B[B]}{k_{2(D)}}$$

The experimental results conform to the above equations, showing that the linear dependence of the product ratios on $[Et_3N] = [B]$ is verified at three different temperatures, with correlation coefficients ranging from 0.93 to 0.99, which is somewhat reassuring in view of the approximations made (Figure 1). The time allowed for the occurrence of interannular shifts before quenching of the arenium ions by the base can be calculated, according to approximation (i) by the ADO theory[26] taking $k_B = k_{\text{collision}}$. In this way, one can evaluate $k_{2(H)}$ and $k_{2(D)}$ at different temperatures and hence the Arrhenius parameters (Figure 2) for the $H^+(D^+)$ interannular shifts. The results are compared in Table II with those concerning *thermal* 1,2 $H^+(D^+)$ shifts in *p-tert*-butyltoluenium ions.[4] The two sets of data are not strictly homogeneous, since the toluene experiments involved only a single D atom, in contrast to the fully deuterated ring of DPE, which could introduce kinetic differences owing to secondary isotope effects. Nevertheless, the comparison is mechanistically informative, allowing inter alia a better definition of the reaction centers involved in the interannular shift. The data of Table II show that 1,2 shifts over the *tert*-butyltoluenium ion are considerably faster than interannular shifts in the whole temperature range investigated. Assuming that 1,2 $H^+(D^+)$ shifts in intermediate **2i**(*p*) occur at the same rate as in *p-tert*-butyltoluenium ion, which is a reasonable assumption in view of the closely similar activating effect of the Me and of the $CH_2CH_2C_6H_5$ substituents, it is reasonable to suppose that the interannular $H^+(D^+)$ shift does not involve the ipso-substituted ion **2i**(*p*) but is preceded by conversion of the latter into ion **2**, namely, that the proton (deuteron) migrates from positions 2, 3, 5, or 6 of the alkylated ring to positions 2′, 4′, or 6′ of the spectator ring.



The Arrhenius parameters and the H/D KIE for the intraannular and for the interannular $H^+(D^+)$ shifts are remarkably close, except for the significantly lower preexponential factor of the latter process. This is not unexpected, since interannular proton transfer requires that the two rings are placed in the specific conformation consistent with the geometric constraints of the transition state. The KIE of H^+ vs D^+ interannular transfer is ≈4.5 ± 2 at 47 °C. This is remarkably similar to the KIE found in metastable

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[25] Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley, New York, 1980.

[26] Bowers, M. T.; Su, T. In *Interactions between Ions and Molecules*; Ausloos, P., Ed.; Plenum Press: New York, 1975; p 163.

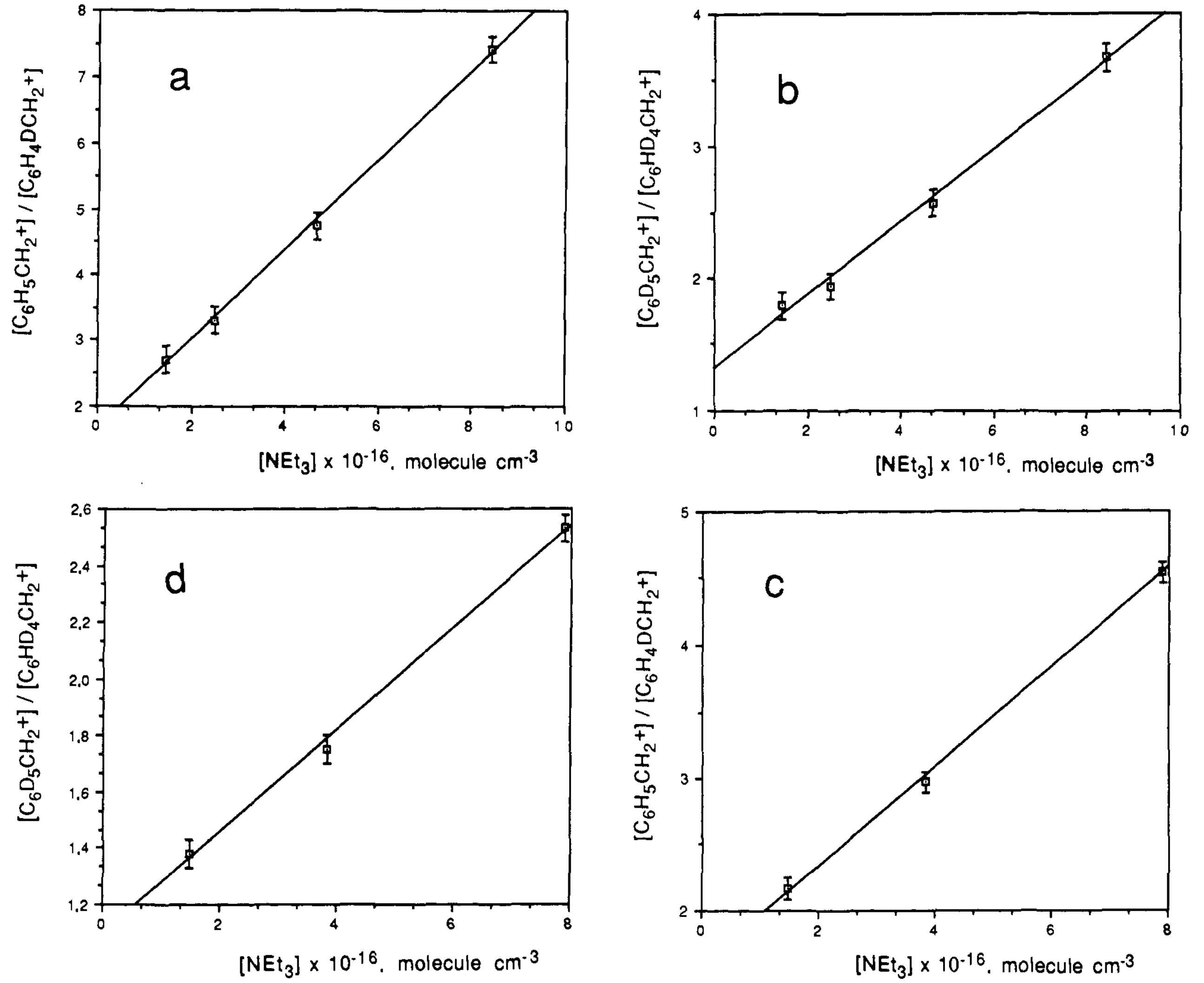
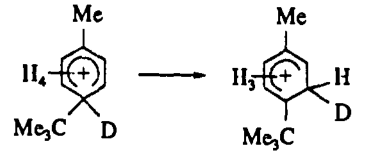
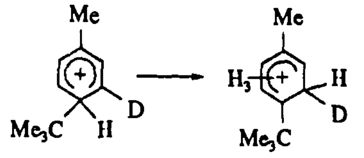
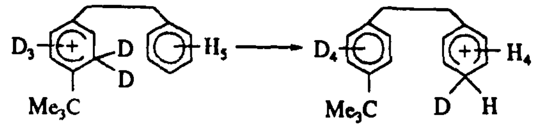
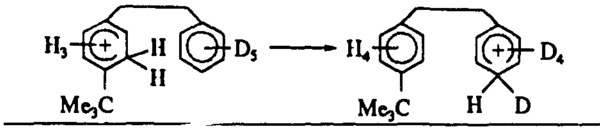


Figure 1. Dependence of the interannular H/D transfer on [Et_3N]: (a) D^+ transfer, 120 °C; (b) H^+ transfer, 120 °C; (c) D^+ transfer, 150 °C; (d) H^+ transfer, 150 °C.

Table II. Kinetic Parameters of Thermal Intraannular and Interannular $H^+(D^+)$ Shifts in Gaseous Arenium Ions

process	log A	E_a, kcal mol^{-1}	k (47 °C), s^{-1}	ref
	12.9 ± 0.4	7.6 ± 0.2	(5.2 ± 0.2) × 10^7	4
		(6.2)[a]	(4.4 ± 2.3) × 10^8	4
	11.9 ± 0.3	8.0 ± 0.2	(2.9 ± 0.6) × 10^6	this work
	11.4 ± 0.4	6.3 ± 0.2	(1.3 ± 0.4) × 10^7	this work

[a] Estimated from k at 47 °C using the same value of A as for the D^+ 1,2 shift, $10^{12.9}$.

$C_6H_5CH_2CH_2C_6H_6^+$ ions (KIE ≈ 5).[17]

No Arrhenius parameters for interannular H^+ shifts in (ω-phenylalkyl)arenium ions occurring in solution are available for comparison with the present gas-phase results. The E_a values for *intermolecular* proton exchange between activated arenes such as *m*-xylene and mesitylene and their conjugate acids in liquid HF have been reported to be 7.5 and 8.0 $kcal^{-1}$, with log A values of 10 and 11, respectively.[27] It is apparent that the activation

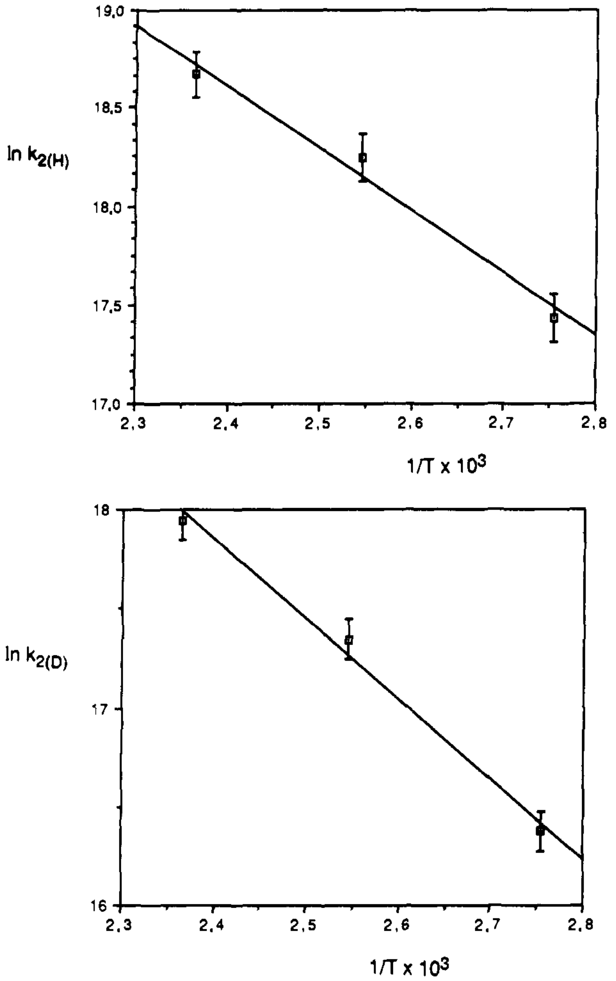


Figure 2. Arrhenius plot showing the dependence of $k_{2(\mathrm{H})}$ and $k_{2(\mathrm{D})}$ on the temperature in the range of 90–150 °C.

energies are similar in solution and in the gas phase, whereas the preexponential factors of the interannular H^+ shifts measured in the gas phase are higher. Despite the different substrates involved and the different reaction environment, it is tempting to trace the higher *A* values of the interannular process to the large effective concentration of the spectator ring, which would amount to 10^2–10^3 mol L^{-1}, based on the *A* values of intermolecular proton exchanges in solution.

The Kinetic Role of the Ion–Molecule Complex. Comparison of the kinetic features of the gas-phase *tert*-butylation of toluene and of DPE, particularly as concerns their relative reactivity and their H/D KIE, provides convincing evidence for the role of the electrostatic, or π-complex **1**, previously inferred from the radiolytic study of aromatic nitration,[28] as well as from the results of mass spectrometric investigations on the reaction of Me_2Cl^+ with toluene[19] and of Me_3C^+ with α,ω-diphenylalkanes.[14a] The overall KIE in the *tert*-butylation of toluene, reflected by a $k_{C_7H_8}/k_{C_7D_8}$ = 1.5 at 120 °C, has been traced to the competition between back dissociation of **2i** (Scheme I) and its conversion into **2** via 1,2 $H^+(D^+)$ shifts, which becomes slower when the heavier isotope is involved.[4] This implies not only that **2i** undergoes significant back dissociation into **1** but that the latter is prone, in turn, to dissociation yielding, free Me_3C^+. For toluene this means that k_{-c} is not negligible with respect to k_1 in the temperature range of interest. In this framework, the observed higher reactivity of DPE than of toluene becomes mechanistically crucial. The $k_{\mathrm{DPE}}/k_{\mathrm{toluene}}$ ratio, 2.9, that may appear small on an absolute scale, is on the contrary quite significant by the standards that apply to exoergic gas-phase alkylation, e.g., *m*-xylene undergoes *tert*-butylation only 1.5 times faster than toluene.[12] The higher reactivity of DPE than of toluene can hardly be traced to a higher activation of the former substrate, in view of the comparable electron-releasing ability of the $C_6H_5CH_2CH_2$ and of the CH_3 substituents. Furthermore, the Me_3C^+ addition is reversible in both cases, as suggested by the H/D *interannular* isotopic discrimination of the electrophile, which favors the unlabeled ring of $C_6D_5CH_2CH_2C_6H_5$ by a factor of 1.60–1.65 at 120 °C. A reasonable explanation of the higher reactivity of DPE than of toluene is that whereas the arenium ion **2i** is prone, as is the corresponding intermediate from toluene, to back dissociation into **1**, the latter, at variance with the corresponding complex from toluene, does not dissociate into a free Me_3C^+ cation and the arene, i.e., in the case of DPE, $k_{-c} \ll k_c$ [DPE]. This hypothesis is consistent with the additional stabilizing effect of the spectator ring of DPE, discussed in a previous section. From the kinetic standpoint, assuming in the extreme hypothesis that formation of complex **1** from DPE but not from toluene is irreversible implies that alkylation of the former but not of the latter substrate occurs at the encounter rate, which provides a reasonable explanation to the otherwise puzzling higher reactivity of DPE.

Consistent with the general pattern of gas-phase *tert*-butylation of alkylbenzenes, no ortho substitution occurs in DPE, and the para:$^1/_2$-meta ratio, although appreciably affected by the temperature and the Et_3N concentration, in general exceeds 1. The extent of meta substitution is higher in DPE than in toluene. Again, explanations based on different electronic effects of the substituents on the meta and the para positions seem inadequate. It appears much more likely that the different orientation reflects instead a different stabilizing effect of the spectator ring of DPE on the transition states and of the corresponding intermediates, involved in the meta and in the para substitution, i.e., a kind of intramolecular differential solvation effect.

Conclusion

Application of the radiolytic approach, coupled with appropriate labeling techniques and temperature-dependence studies, has allowed the first kinetic study of *thermal* interannular proton shifts in gaseous (ω-phenylalkyl)arenium ions. The results show that such processes do occur under conditions of purely thermal activation, and their rate is lower by roughly 1 order of magnitude than that of 1,2 intraannular shifts in comparable monocyclic ions. The rate difference reflects the predictably lower preexponential factor in ring-to-ring than in 1,2 proton migration. On the basis of the comparison with the available kinetic information on *intermolecular* proton exchange in solution, the preexponential factor of the interannular shifts in the gaseous bicyclic ions can be taken as indicative of an effective molarity of the spectator ring of 10^2–10^3 mol L^{-1}. This work provides, moreover, a significant addition to the very limited set of data currently available on the occurrence and the extent of kinetic isotope effects in gas-phase ion–molecule reactions. In fact, the interannular hydrogen migration is characterized by a sizeable H/D KIE, comparable in magnitude to those previously observed in 1,2 intraannular $H^+(D^+)$ shifts. As to the latter processes, we note as an aside that additional evidence for their occurrence and kinetic role is provided by the significant isotopic discrimination that characterizes the Me_3C^+ attack on the two rings of $C_6D_5CH_2CH_2C_6H_5$.

Comparison with pertinent mass spectrometric results underlines the unique features of the high-pressure radiolytic technique in the kinetic study of gas-phase ion–molecule reactions. Interannular H/D isotopic scrambling has been detected by mass spectrometric techniques in protonated α,ω-diphenylalkanes containing from 2 to 20 methylene units in the aliphatic chain.[3] By necessity such mass spectrometric observations concern only those arenium ions that are sufficiently excited to undergo metastable benzene loss. In these ions, which obviously contain a large excess of internal energy, equilibration of the 11 hydrogen atoms of the two rings is complete in the 10-μs time window of the mass spectrometric technique used, which establishes only the lower limit ($\sim 10^6$ s^{-1})

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(27) Koptyug, V. A. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1984; Vol. 122, p 119 and references therein.

(28) Attinà, M.; Cacace, F.; Ricci, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1177.

of the interannular proton-transfer rate constants.[7,17,29]

By contrast, the time resolution of the radiolytic technique has extended the range of measurable rate constants up to at least 10^8 s^{-1}. Even more importantly the processes investigated are truly thermal reactions, occurring at a defined temperature and obeying standard thermal kinetics. This not only allows evaluation of Arrhenius activation parameters but also confers the results with a much higher degree of generality, making them legitimately comparable with the corresponding processes occurring in solution.

As a closing remark, it is worth noting that the radiolytic results fully support the conclusions of a recent mass spectrometric study pointing to the formation of stable ion–neutral complexes in the reaction of Me_3C^+ with α,ω-diphenylalkanes.[14a]

Acknowledgment. This research was supported by Ministero per l'Università e la Ricerca Scientifica e Tecnologica (MURST) and by the Italian National Research Council (CNR) and by the Forschungsprojekt 2194/26 of the Universität Bielefeld.

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(29) A rate $\gg 10^6$ s^{-1} follows from the complete equilibration of 16 or even 21 protons in protonated oligophenylalkanes: Kuck, D.; Fastabeud, U. *Adv. Mass Spectrom.* **1989**, *11A*, 904.

Photoelectron Spectroscopy of the Monofluorovinylidene and Difluorovinylidene Anions: The Monofluorovinylidene–Fluoroacetylene Rearrangement

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Received August 21, 1992

Abstract: The 351.1-nm photoelectron spectra of $HFC{=}C{:}^-$ and $F_2C{=}C{:}^-$ are reported. Transitions from the anion ground state to the neutral singlet ground state and low-lying triplet states are observed. The electron affinity of difluorovinylidene is 2.255 (6) eV, and the triplet term energy is $T_0(\tilde{a}\ ^3A_2\ F_2CC)$ = 0.924 (9) eV. In the singlet state of $F_2C{=}C{:}$, vibrational progressions are observed at 510 (25), 905 (25), and 1670 (25) cm^{-1}. Vibrational frequencies of 505 (25) and 800 (35) cm^{-1} are observed in the difluorovinylidene anion. The adiabatic electron affinity of monofluorovinylidene is 1.718 (6) eV, and the triplet term energies are $T_0(\tilde{a}\ ^3A''\ HFCC)$ = 1.320 (9) eV and $T_0(\tilde{b}\ ^3A'\ HFCC)$ = 1.358 (9) eV. Vibrational fundamentals are observed at 205 (30), 960 (30), and 1680 (30) cm^{-1} in the $\tilde{X}\ ^1A'$ state of $HFC{=}C{:}$, at 600 (50) and 1100 (100) cm^{-1} in the $\tilde{b}\ ^3A'$ state, and at 485 (30) and 710 (35) cm^{-1} in the negative ion ($\tilde{X}\ ^2A'$). Ab initio calculations indicate that the normal mode primarily involved in the hydrogen migration to form fluoroacetylene from monofluorovinylidene is the CCF bending mode. By modeling the observed CCF bending mode as an anharmonic oscillator, we estimate the hydrogen isomerization barrier height to be 2 ± 1 kcal/mol.

Introduction

Negative ion photodetachment spectroscopy has been used in several ways to probe transition states and unstable species. The transition states of the hydrogen abstraction reactions X + HY (X = F, Cl, Br, Y = Cl, Br, I) have been probed by photodetachment of XHY^- species by Bradforth et al.[1] and Metz et al.[2] Moylan et al.[3] measured the photodetachment threshold of several ROHY species (R = $C_6H_5CH_2$ and CH_3, Y = F^- and OCH_3^-) to determine the well depth for proton transfer between RO^- and HY using a thermochemical cycle. An early study of the vinylidene anion revealed vibrational structure in the photoelectron spectrum of singlet vinylidene, which readily isomerizes to acetylene.[4] In a more recent study from this laboratory,[5] photodetachment of the vinylidene anion accessed the very shallow well of the ground neutral state of vinylidene, and information about the rearrangement barrier was obtained from the analysis of the vibrational structure in the spectrum. The lifetime of the $\tilde{X}\ ^1A_1$ state of vinylidene against rearrangement was found to be 0.04–0.2 ps.

In this study the photodetachment spectra of monofluorovinylidene ($HFC{=}C{:}^-$) and difluorovinylidene ($F_2C{=}C{:}^-$) anions are reported. Figure 1 shows schematic molecular orbital diagrams for the electronic states of the vinylidenes with symmetry labels. Since difluorovinylidene and vinylidene are both C_{2v}, they have the same symmetry labels; the symmetry labels for monofluorovinylidene (C_s) are slightly different. The singlet states arise from detachment of an electron from the in-plane terminal carbon p (b_2) orbital of the anions. There are two low-lying triplet states. The $^3B_2$ ($^3A'$) states arise from photodetachment from the carbon lone-pair (a_1) orbital of the anion. The $^3A_2$ ($^3A''$) triplet arises from photodetachment of an electron from the C–C π-bond of the anion or from the singlet neutral ground state via a b_1 (π) → b_2 (p) excitation. In vinylidene the $\tilde{a}\ ^3B_2$ state is the lowest energy triplet. The ordering of the triplet states in monofluorovinylidene and difluorovinylidene are determined in this work.

There are several recent calculations on the fluorovinylidene species. New high-level calculations on monofluorovinylidene by DeLeeuw et al.[6] include geometry and frequency optimization on the ground-state singlet and anion. The transition-state geometry

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