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 $1 \times 10^{-10}$ 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 $>10^4$ 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 samples were mounted on 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 $\sim 2$ 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 $\sim 1200$ K by a tungsten filament or cooled to $\sim 100$ 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 vms contamination in the effluent. Gas exposures were not corrected for the varying sensitivities of the different ionization gauges.

Acknowledgment. We thank R. S. Freund (AT&T Bell Laboratories), J. Parmeter (Sandia National Laboratories), and A. Jain and T. T. Koda (University of New Mexico) for communicating results prior to publication. We also thank B. R. Zegarski for help in collecting some of the infrared data. G.S.G. acknowledges support from the Department of Energy under contract DEFG02-91ER45439 and is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Award and an A. P. Sloan Foundation Research Award. P.M.J. acknowledges the receipt of a University of Illinois Department of Chemistry Fellowship.

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

Fulvio Cacace,*1 Maria Elisa Crestoni,1 Simonetta Fornarini,1 and Dietmar Kuck1

Abstract: The first demonstration of thermal interannular proton shifts in gaseous bicyclic arenium ions and the evaluation of their Arhenius parameters have been achieved with the radiolytic technique. The model ions have been obtained by alkylation of C$_6$D$_5$CH$_2$CH$_2$C$_6$H$_5$ with radiolytically formed Me$_2$C$^+$ 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 monocyclic arenes, the rate constant for the H$^+$ ring-to-ring transfer in the para-substituted arenium ions has been estimated to be $(1.3 \pm 0.4) \times 10^9$ (2.9 ± 0.6) $\times 10^8$ 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$^+$ 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$_2$C$^+$, which favors the unlabelled ring of C$_6$D$_5$CH$_2$CH$_2$C$_6$H$_5$, is explained by a factor of 1.7 at 47°C, consistent with the formation of stable complexes between Me$_2$C$^+$ and a,a-di-diphenylethanes.

Proton shifts in aromatic systems have been the subject of extensive studies by NMR techniques in acid solutions and by computational methods. Their occurrence in gaseous arenium ions is well documented by the (chemical ionization (CI)) and ion cyclotron resonance (ICR) mass spectrometric investigations. A kinetic study was recently reported of 1.2 proton shifts in gaseous arenium ions based on the radiolytic technique, which

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1. Università "La Sapienza".
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(b) Koptyug, V. A. In Contemporary Problems in Carbonium Ions Chemistry III; Rees, Ch., Ed.; Springer-Verlag, Berlin, 1984; p 119 and references therein.
whose protonated adduct has been shown by mass spectrometric techniques to undergo extensive interannular hydrogen migration. The charged alkylating agent used is a regular, place, the time resolution allowed by the radiolytic technique, of occurrence. Under such conditions, hardly accessible to mass spectrometric approaches, 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 areonium ions. The unique features of the radiolytic technique, complemented by isotope labeling and temperature-dependence experiments, have allowed the derivation of Arrhenius parameters of 1,2 proton shifts in substituted benzene 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 (p-phenylethyl) areonium ions from the cationic alkylation of 1,2-diphenylethylene (DPE), the most simple o,ω-diphenylalkane whose protonated adduct has been shown by mass spectrometric techniques to undergo extensive interannular hydrogen migration.5,6 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 10⁻⁵ ms time frame of the mass spectrometric experiments.6 The charged alkylating agent used in this work, MeO⁺, 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.8-10 In particular, the reaction of MeO⁺ with selectively deuterated toluenes has been used to obtain the gaseous areonium ions whose 1,2 proton shifts have been studied with the radiolytic technique,4 whereas its reactions with simple alkylbenzenes and o,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: MeO⁺ ions from the radiolysis of i-C₆H₁₀ are allowed to react with C₆H₄CH₂CH₂C₆D₅ in isobutane gas at pressures ranging from 630 to 1730 Torr. The areonium ions from the cationic alkylation are eventually deprotonated by Et,N, yielding as the end product a mixture of isomeric (2-phenylethyl)-2,6-t-butylbenzenes whose yields, isomeric composition, and intramolecular D distribution are determined by GC MS. The lifetime of the areonium ions and hence the time allowed for the occurrence of intramolecular proton shifts before quenching by Et₂N 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-C₆H₁₀, CH₄, and O₂ were research-grade gases from Matheson Co. with a stated purity exceeding 99.98 mol %. Most other chemicals used, including toluene and 1,2-diphenylethylene, were obtained from commercial sources. C₆H₅CH₂CH₂C₆D₅ 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.1 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 × 10⁴ to 2 × 10⁵ Gy at a dose rate of 2 ± 0.5 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 0.5-μm cross-linked

<table>
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<th>system composition (Torr) *</th>
<th>1,2-di-phenyl- ethylene</th>
<th>triethyl- amine</th>
<th>i-C₆H₁₀</th>
<th>t, °C</th>
<th>meta</th>
<th>para</th>
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<td>690 ± 40</td>
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<td>630 ± 40</td>
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<th>isotopic composition a</th>
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<th>MeO⁺C₆H₅C₆D₅, CH₄</th>
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<table>
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<tr>
<th>isotopic composition a</th>
<th>MeO⁺C₆H₅C₆D₅, CH₃</th>
<th>MeO⁺C₆H₅C₆D₅, CH₄</th>
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</thead>
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<td>14.0 ± 0.4</td>
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</table>

* All gaseous systems contained O₂ (10 Torr) as a radical scavenger. Standard deviation ± 10%. The system contained, in addition, toluene (0.66 Torr). The competition gave a k_{DPE}/k_{CH₄} ratio of 2.9 ± 0.3.
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 ionizing character of the alkylation is ensured by a large excess (10 Torr) of O₂, an effective radical scavenger, and is independently confirmed by the depression of the yields caused by the presence of a gaseous base (Et₃N) which efficiently intercepts the Me₃C⁺ 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 Et₃N, 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-butylidiphenylmethanes display as the base peak (100%) the Me₃C-C₆H₄⁺ tert-butyldiphenylmethyl benzyl ion, m/z = 147, together with the molecular ion at m/z = 238 (ca. 40%) and the C₆H₄⁺ unsubstituted benzyl ion at m/z = 91 (ca. 30%). The molecular ions of the deuterated tert-butyldiphenylmethanes from the alkylation of C₆D₅CH₂CH₂C₆H₅ 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 Me₃C⁺ ions. This ratio, reported in Table I, allows one to estimate the relative rate of alkylation of the unlabeled and of the fully deuterated rings, 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 C₆D₅CH₂CH₂C₆H₅ displays equal abundances of C₆D₅CH₂⁺ and C₆H₄CH₂⁺ ions without detectable amounts of isotopically mixed fragments, such as C₆HD₃CH₂⁺, C₆H₂D₂CH₂⁺, etc., indicative of interannular H/D scrambling induced by the ionization process. Such a feature sets DPE apart from the higher α,ω-diphenylalkanes, 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 benzyl fragment ions, and allows GC-MS to be used for evaluating the intramolecular D distribution in the alkylated products.

On the basis of the above considerations, the ratios of the abundances of ions of types A and B in each family of Me₆C-C₆X₂CH₂⁺ and of C₆X₂CH⁺ ions, 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 C₆D₅CH₂CH₂C₆H₅ rings is different, being higher for the unlabeled ring under all reaction conditions examined. The ratio of alkylation on the C₆H₅ compared to the C₆D₅ 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 Et₃N, 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 Et₃N, the para/ 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 [Et₃N] leads to a significant enhancement of para substitution, e.g., at 120 °C the para/m meta ratio increases from 1.17 in the absence of added bases to 2.00 in the presence of 5.72 Torr of Et₃N. 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-butylation ring to the unsubstituted ("spectator") ring of DPE is provided by the C₆D₅CH₂⁺/C₆H₄CH₂⁺ and by the C₆H₂D₃CH₂⁺/C₆H₃DCH₂⁺ abundance ratios in the EI mass spectra of the tert-butylated 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 C₆D₅CH₂⁺/C₆H₄CH₂⁺ and the C₆H₂D₃CH₂⁺/C₆H₃DCH₂⁺ 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 Et₃N. In the EI mass spectra of the tert-butylation products, the detection of Me₆C-C₆D₅CH₂⁺, and of Me₆C-C₆D₅CH⁺ ions, in addition to the isotopically intact Me₆C-C₆D₅CH⁺ and Me₆C-C₆D₅CH₂⁺ 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 Me₆C-C₆D₅CH₂⁺/Me₆C-C₆D₅CH⁺ and the Me₆C-C₆D₅CH₂⁺/Me₆C-C₆D₅CH⁺ ratios show a more pronounced dependence on [Et₃N] than the corresponding C₆D₅CH₂⁺/C₆HD₃CH₂⁺ and C₆H₂D₃CH₂⁺/C₆H₃DCH₂⁺ ratios.

**Discussion**

**General Mechanistic Features of Gas-Phase Aromatic tert-Butylation.** Gaseous Me₆C⁺ 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.17,18-13 The general mechanistic picture of the gas-phase aromatic alkylation by thermal Me₆C⁺ 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 I, thermalized by unreactive collisions in the dense bath gas, 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 ≥10⁶ s⁻¹.
Scheme I

\[
\begin{array}{c}
\text{Me}_3C^+ + \text{ArH} \xrightarrow{k_1} [\text{Me}_3C^+\text{-ArH}]^- \\
\xrightarrow{k_c} \text{Me}_3C^+ + \text{H}^+ + \text{Ar}^-
\end{array}
\]

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 alklylation irreversible. Scheme I can be extended to diphenylalkanes, such as DPE (R = CH₂CH₂Ph), by taking into account two distinctive features of the latter. First, in addition to intrannular proton shifts, the binding energy of the [C₆H₇⁺-C₆H₆] complex, as high as 11 kcal mol⁻¹, and of DPE, 194.6 kcal mol⁻¹, the difference, which is likely to arise from the binding energy of the spectator ring of DPE, which consequently stabilizes both intermediates.

An important factor which controls the rate of intrannular 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 intrannular H⁺ shifts that convert 2i(m) and 2i(p) into more stable protonated species. As in the case of toluene, the sterics requirements of Me₃C⁺ allow alklylation exclusively at the meta and para positions of DPE, yielding the corresponding ipso-substituted ions 2i(m), 2i(p), 2i(m), and 2i(p).

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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 \( < 201 \text{ kcal mol}^{-1} \)) and Et\(_3\)N (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 \( pK_a = 0 \), 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 \( \text{H}^+ (\text{D}^+) \) 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 abundance of the corresponding benzyl ions in their E1 mass spectra:

\[
\frac{[\text{Me}_3\text{C-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5]}{[\text{Me}_3\text{C-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{D}_5]} = \frac{2k_{2(H)}}{k_{2(D)}} \]

\[
\frac{[\text{Me}_3\text{C-C}_6\text{D}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5]}{[\text{Me}_3\text{C-C}_6\text{D}_5\text{CH}_2\text{CH}_2\text{C}_6\text{D}_5]} = \frac{2k_{2(D)}}{k_{2(D)}}
\]

The experimental results conform to the above equations, showing that the linear dependence of the product ratios on \( [\text{Et}_3\text{N}] = [B] \) 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 arenic ions by the base can be calculated, according to approximation (i) by the ADO theory^26 taking \( k_0 = k_{\text{collision}} \). In this way, one can evaluate \( k_{2(H)}^0 \) and \( k_{2(D)}^0 \) 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-butyltoluene 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-butyltoluene 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-butyltoluene ion, which is a reasonable assumption in view of the closely similar activating effect of the Me and of the \( \text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \) 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 \(-4.5 \pm 2\) at 47 °C. This is remarkably similar to the KIE found in metastable


Intraannular Proton Shifrs in Thermal Arenium Ions

$[\text{NE}_3] \times 10^{-6}$, molecule cm$^{-3}$

Figure 1. Dependence of the interannular H/D transfer on [Et$_3$N]: (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

<table>
<thead>
<tr>
<th>Process</th>
<th>$\log A$</th>
<th>$E_a$, kcal mol$^{-1}$</th>
<th>$k$ (47 °C), s$^{-1}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me} \quad \text{Me}$</td>
<td>$\text{Me}$</td>
<td>12.9 ± 0.4</td>
<td>7.6 ± 0.2</td>
<td>$(5.2 ± 0.2) \times 10^7$</td>
</tr>
<tr>
<td>$\text{Me} \quad \text{Me}$</td>
<td>$\text{Me}$</td>
<td>$(6.2)^t$</td>
<td>$(4.4 ± 2.3) \times 10^6$</td>
<td>4</td>
</tr>
<tr>
<td>$\text{Me} \quad \text{Me}$</td>
<td>$\text{Me}$</td>
<td>$11.9 ± 0.3$</td>
<td>$8.0 ± 0.2$</td>
<td>$(2.9 ± 0.6) \times 10^6$</td>
</tr>
<tr>
<td>$\text{Me} \quad \text{Me}$</td>
<td>$\text{Me}$</td>
<td>$11.4 ± 0.4$</td>
<td>$6.3 ± 0.2$</td>
<td>$(1.3 ± 0.4) \times 10^7$</td>
</tr>
</tbody>
</table>

$^t$Estimated from $k$ at 47 °C using the same value of $A$ as for the D$^+$ 1,2 shift, $10^{120}$.

$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4^{+}$ ions (KIE = 5).$^{17}$

No Arrhenius parameters for interannular H$^+$ shifts in ($\omega$-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
The kinetic role of the ion-molecule complex. Comparison of the kinetic features of the gas-phase tert-butylolation 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. 

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. 

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 monocationic ions. The rate difference reflects the predictably lower preexponential factor in ring-to-ring than in 1,2 proton migration. On the basis of our comparison with the available kinetic information on intramolecular 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 10^7–10^10 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 MeC^+ attack on the two rings of C_6D_5CH_2CH_2C_6H_4.

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. 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 (~10^6 s^-1)
of the interannular proton-transfer rate constants.\textsuperscript{17,29}

By contrast, the time resolution of the radiolytic technique has extended the range of measurable rate constants up to at least $10^6$ 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 MeC\(^+\) with $\alpha$, $\omega$-diphenylalkanes.\textsuperscript{164}

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.

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

Mary K. Gilles, W. C. Lineberger, and Kent M. Ervin

Abstract: The 351.1-nm photoelectron spectra of HFC\(=\)C\(^-\) and F\(_2\)C\(=\)C\(^-\) are reported. Transitions from the anion ground state to the neutral singlet ground state and lowest-lying triplet state are observed. The electron affinity of difluorovinylidene is 2.255 (6) eV, and the triplet term energy is $T_d(\tilde{A}\,^3\,A_2, \, F_2CC) = 9.924 (9)$ eV. In the singlet state of F\(_2\)C\(=\)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 $T_d(\tilde{A}\,^3\,A', \, HFCC) = 1.320 (9)$ eV and $T_d(\tilde{B}\,^3\,A', \, HFCC) = 1.358 (9)$ eV. Vibrational fundamentals are observed at 205 (30), 960 (30), and 1680 (30) cm\(^{-1}\) in the $\tilde{X}\,^1\,A'$ state of HFC\(=\)C\(^-\), at 600 (50) and 1100 (100) cm\(^{-1}\) in the $\tilde{B}\,^3\,A'$ state, and at 485 (30) and 710 (35) cm\(^{-1}\) in the negative ion ($\tilde{X}\,^2\,A'$). 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 Bradford et al.\textsuperscript{2} and Metz et al.\textsuperscript{3} Moylan et al.\textsuperscript{4} measured the photodetachment threshold of several ROHY species (R = C\(_6\)H\(_5\), CH\(_3\), CH\(_3\)CO, Y = F and OCH\(_3\)) to determine the well depth for proton transfer between RO and HY using a theromchelical cycle. An early study of the vinylidene anion revealed vibrational transitions in the photoelectron spectrum of singlet vinylidene, which readily isomerizes to acetylene.\textsuperscript{5} In a more recent study from this laboratory,\textsuperscript{6} 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 $\tilde{X}\,^1\,A'$ 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\(_2\)C\(=\)C\(^-\)) anions are reported. Figure 1 shows schematic molecular orbital diagrams for the electronic states of the vinylidene with symmetry labels.

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\textsuperscript{2}University of Nevada.

\begin{itemize}
\item[(2)] Metz, R. B.; Weaver, A.; Bradford, S. E.; Kissopoulos, T. N.; Neumark, D. M. J. Phys. Chem. 1990, 94, 1377.
\end{itemize}