

# Proton Shifts in Gaseous Arenium Ions and Their Role in the Gas-Phase Aromatic Substitution by Free $\text{Me}_3\text{C}^+$ and $\text{Me}_3\text{Si}^+$ Cations

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**Abstract:** The gas-phase reaction of  $\text{Me}_3\text{C}^+$  with benzene and toluene has been studied at 720 Torr, in the temperature range from 47 to 120 °C with the radiolytic technique, using suitably deuterated substrates. The results underline the kinetic role of the 1,2-H(D) shifts in the primary charged intermediate, the  $\sigma$  complex I. When the latter originates from  $\text{Me}_3\text{C}^+$  attack at the para position of  $p\text{-MeC}_6\text{H}_4\text{D}$ , the D shift rate is relatively slow, ca.  $5 \times 10^7 \text{ s}^{-1}$  at 47 °C, with an activation energy  $E_a = 7.6 \pm 0.2 \text{ kcal mol}^{-1}$  and a preexponential factor  $A = 10^{12.9 \pm 0.4}$ . Ions I from the  $\text{Me}_3\text{C}^+$  attack on benzene or at the meta positions of toluene have lifetimes shorter than a few nanoseconds, and the 1,2-H shift, while still kinetically significant in the overall benzene reaction, is unaffected by addition of strong bases to the gas at pressures up to 8 Torr, which ensures deprotonation of I within 1 ns. Since 1,2-H(D) shifts compete with back dissociation of I, their rate influences the net alkylation rate, which accounts for the kinetic isotope effect in excess of 2 observed in the competitive *tert*-butylation of  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$ , the first one reported for a *thermal* ionic reaction in the gas phase. Analogous experiments involving the reaction of  $\text{Me}_3\text{Si}^+$  with benzene and toluene show that H(D) shifts are remarkably slow from the ipso-silylated position, consistent with its high site basicity demonstrated by previous mass spectrometric and radiolytic studies.

The study of electrophilic aromatic substitution in the gas phase is of considerable interest, since it allows one to establish the intrinsic features of this important class of reactions, unperturbed by the effects of the medium so pronounced in condensed systems. Full exploitation of gas-phase approaches and meaningful kinetic correlation with solution chemistry presupposes, however, overcoming certain peculiar problems of gas-phase ion-molecule interactions. Of particular concern is the "electrostatic activation" occurring in the low-pressure domain, where inefficient collisional thermalization allows the energy released by the electrostatic ion-molecule interaction to remain stored in the degrees of freedom of the collision complex formed, with important kinetic consequences. First, it is impossible to define a kinetically meaningful temperature. Furthermore, the excess internal energy can allow the collision complex to overcome the activation barrier of the reaction, i.e., referring to the general outline of aromatic substitution reactions given in Scheme I,  $k_1 > k_{-c}$ , and the collision complex ( $\text{ArH} \cdot \text{E}^+$ ) evolves into the  $\sigma$  complex I, in all events.<sup>1</sup> In this case the substitution displays no selectivity, since the experimentally observed relative reactivities nearly reflect relative collision rates (Scheme I). The problem can be overcome by working in a bath gas sufficiently dense to allow collisional thermalization of the ( $\text{ArH} \cdot \text{E}^+$ ) complex *before* its conversion into I. Moreover, formation of the collision complex is less exothermic in a dense gas than under isolated-pair conditions since  $\text{E}^+$  is likely to be associated with a bath-gas molecule M, so that the energy released in the process



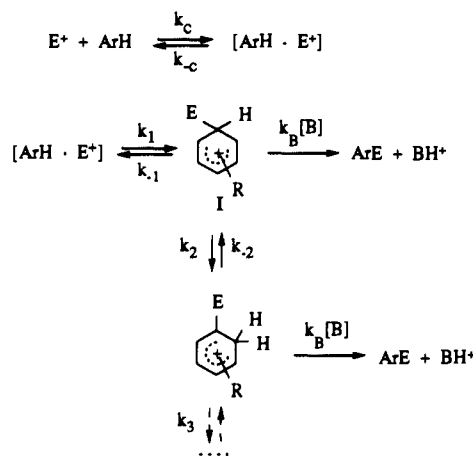
amounts only to the difference between the binding energies of the ion  $\text{E}^+$  to  $\text{ArH}$  and to M. As a typical example, the collision frequency of a ( $\text{Me}_3\text{C}^+ \cdot \text{C}_6\text{H}_6$ ) complex in isobutane at 40 °C and 760 Torr is of the order of  $5 \times 10^{10} \text{ s}^{-1}$ , and more than 40% of the  $\text{Me}_3\text{C}^+$  ions are present as ( $\text{Me}_3\text{C}^+ \cdot i\text{-C}_4\text{H}_{10}$ ) complexes.<sup>2</sup>

The pressure required to achieve thermalization of the collision complex, the "high-pressure limit" above which ion-molecule reactions obey thermal kinetics, depends of course on the specific system studied, but in general it exceeds by orders of magnitude the pressure range accessible to current mass spectrometric techniques.

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Scheme I



Therefore, most of the kinetic data on *thermal* aromatic substitutions by gaseous cations have been obtained with the radiolytic technique, characterized by a pressure range up to several atmospheres and allowing direct evaluation of the substrate and positional selectivity of the substitution by direct isolation and characterization of the isomeric end products.<sup>1</sup> Many of the charged electrophiles so far studied in the gas phase, e.g., the lower carbenium ions, display a very high reactivity by solution chemistry standards, reflecting the lack of a solvation shell and of a counterion.<sup>3</sup> As a consequence, there is a low activation barrier to the  $\sigma$  complex,  $k_1 > k_{-c}$  in Scheme I, and the reaction occurs at the encounter rate, lacking substrate and positional discrimination, e.g., alkylation by the ethyl cation in methane at atmospheric pressure is characterized by a  $k_{\text{toluene}}/k_{\text{benzene}}$  ratio of ca. 0.8, with a para/<sup>1</sup>/<sub>2</sub> meta ratio as low as 1.3 at 37.5 °C.<sup>3a</sup>

The above considerations explain the quest for less reactive cations and the special interest attached to  $\text{Me}_3\text{C}^+$ , whose relatively mild electrophilic character and the stringent steric requirements

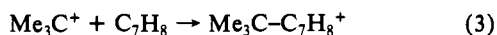
(3) (a) Cacace, F.; Cipollini, R.; Giacomello, P.; Possagno, E. *Gazz. Chim. Ital.* 1974, 104, 977. (b) Cacace, F.; Possagno, E. *J. Am. Chem. Soc.* 1973, 95, 3397. (c) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* 1977, 99, 2611. (d) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Chem. Soc., Perkin Trans. 2* 1979, 891. (e) Attinà, M.; Giacomello, P. *J. Am. Chem. Soc.* 1979, 101, 6040. (f) Aliprandi, B.; Cacace, F.; Fornarini, S. *Tetrahedron* 1987, 43, 2831. (g) Cerichelli, G.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* 1992, 114, 2002.

endow its reaction with arenes with the required sensitivity to the effects of substituents and to structural changes of the substrate.

Gas-phase aromatic *tert*-butylation has been the focus of extensive mass spectrometric and radiolytic studies.<sup>4</sup> Formation of *tert*-butylated  $\sigma$  complexes from benzene is well documented by pulsed high-pressure mass spectrometry in the pressure range up to 4 Torr.



Kebarle et al. have reported  $\Delta H^\circ_2 = -22 \pm 2$  kcal mol<sup>-1</sup> and  $\Delta S^\circ_2 = -49 \pm 5$  cal K<sup>-1</sup> mol<sup>-1</sup>, assigning the ionic product the 4-protonated *tert*-butylbenzene structure.<sup>5</sup> These data have been confirmed in a recent study by Stone and Stone,<sup>6</sup> who have examined, in addition, the alkylation of toluene,



assigning the charged product the 4-, or 6-protonated 3-*tert*-butyltoluene structure and measuring both  $\Delta H^\circ_3 = -29.1 \pm 0.3$  kcal mol<sup>-1</sup> and  $\Delta S^\circ_3 = -54.6 \pm 0.8$  cal K<sup>-1</sup> mol<sup>-1</sup>. Neither value changes appreciably in passing from C<sub>7</sub>H<sub>8</sub> to C<sub>7</sub>D<sub>8</sub>, and the *tert*-butylated adduct from the latter has been found to transfer a deuteron to gaseous bases, consistent with the suggested arenium ion structure.<sup>6</sup>

Radiolytic experiments, carried out in isobutane and neopentane at atmospheric pressure, have provided pertinent kinetic information.<sup>4</sup> At 37.5 °C Me<sub>3</sub>C<sup>+</sup> ions display a remarkable substrate discrimination, measured by a  $k_{\text{toluene}}/k_{\text{benzene}}$  ratio of  $55 \pm 5$ , unusually high for a gaseous cation and even *higher* than in conventional Friedel-Crafts *tert*-butylation reactions.<sup>4a</sup> The orientation is also selective, e.g., in toluene there is no detectable ortho substitution, and the *para*/<sup>1</sup>/<sub>2</sub> *meta* ratio is ca. 35. From the Arrhenius plot of the  $k_{\text{toluene}}/k_{\text{benzene}}$  ratio, obtained from a temperature-dependence study in isobutane at 720 Torr, a  $3.6 \pm 0.4$  kcal mol<sup>-1</sup> difference between the activation energies for the *tert*-butylation of benzene and of toluene has been estimated.<sup>4a</sup>

On the basis of these results, the present study is aimed at elucidating the detailed course of aromatic substitution by gaseous Me<sub>3</sub>C<sup>+</sup> ions, especially as regards the factors influencing the competition between back dissociation of the ipso-substituted arenium ion I and its evolution into the products. Since the competition depends to a large extent on the rapidity of the proton shifts from the ipso carbon to other ring positions, a major objective of this study is the evaluation of the rate constants of proton migrations in gaseous arenium ions, a subject of considerable intrinsic interest, currently the focus of numerous experimental and theoretical investigations.<sup>7</sup> Finally, isotopic labeling techniques, in particular the study of deuterated arenes, allow evaluation of kinetic H/D isotope effects in proton migration and of their influence on the net alkylation rate. The information obtained is by no means irrelevant since, despite the widespread use of deuterated reactants in mass spectrometry, preciously little is known on H/D kinetic isotope effects (KIEs) in gas-phase ion-molecule reactions obeying thermal kinetics, the only ones amenable to standard quantitative treatments and comparable to KIEs in solution.

The study has been extended to the closely related aromatic substitution by gaseous Me<sub>3</sub>Si<sup>+</sup> ions, which provides a useful comparison term, owing to the widely different effects of the Me<sub>3</sub>C and Me<sub>3</sub>Si groups on the basicity of the ipso carbon relative to

adjacent ring positions and hence on the rate of the proton shifts in ipso-*tert*-butylated (I, E = Me<sub>3</sub>C) and ipso-trimethylsilylated (I, E = Me<sub>3</sub>Si) arenium ions.

## Experimental Section

**Materials.** *i*-C<sub>4</sub>H<sub>10</sub>, CH<sub>4</sub>, and O<sub>2</sub> were research grade gases from Matheson Co. with a stated purity in excess of 99.95 mol %. Most of the other chemicals used, including perdeuterated benzene and toluene, whose isotopic purity exceeded 99.96%, were commercial products from Aldrich Chimica S.r.l. or Fluka Chemie AG. Exceptions were *o*-, *m*-, and *p*-deuteriotoluenes, which were synthesized from the corresponding bromotoluenes, preparing the Grignard reagents in carefully dried ether, followed by hydrolysis with D<sub>2</sub>O. The deuterated toluenes were isolated and purified by preparative GLC, using a 4-m-long column packed with Carbowax 20M-KOH (2%) on Supelcoport. The synthesis yielded a deuterium incorporation of  $85 \pm 2\%$ ,  $60 \pm 2\%$ , and  $73 \pm 2\%$  into the *p*-, *m*-, and *o*-deuteriotoluenes, respectively. The D content was determined by CH<sub>4</sub> chemical ionization mass spectrometry, comparing the intensities of [M + C<sub>2</sub>H<sub>5</sub>]<sup>+</sup> ions after correction of the <sup>13</sup>C contribution, using a Hewlett-Packard 5892A quadrupole instrument. An independent determination of the D content was obtained by <sup>13</sup>C-NMR spectrometry. In the proton-decoupled <sup>13</sup>C-NMR spectra, the aromatic <sup>13</sup>C bearing the D atom is characterized by an isotope effect on the chemical shift and by a triplet absorption pattern with <sup>1</sup>J<sub>13C-D</sub> ≈ 24 Hz. The integrated triplet signal was checked against that of the corresponding H-bearing <sup>13</sup>C to obtain the relative amounts of CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>D versus CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>. The NMR spectra were recorded on a Varian XL 300 instrument with a <sup>13</sup>C probe operating at 75.43 MHz.

**Radiolytic Experiments.** The gaseous samples were prepared using standard vacuum procedures in sealed 135-mL Pyrex vessels.<sup>1b</sup> The competition experiments involving C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>D<sub>6</sub> and CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>-CD<sub>2</sub>C<sub>6</sub>D<sub>5</sub> mixtures required a precise knowledge of the relative amounts of deuterated and undeuterated reactants. To this end, a calibrated stock mixture was prepared, from which the required amount for each experiment of the series was weighed. The irradiations were carried out in a 220 Gammacell (Nuclear Canada Ltd.) at total doses ranging from  $1 \times 10^4$  Gy to  $2 \times 10^4$  Gy at a dose rate of ca.  $2 \times 10^4$  Gy h<sup>-1</sup>. The radiolytic products mixture was extracted by freezing the vessel to 77 K and then washing its inner walls with ethyl acetate with repeated freeze-thaw cycles. The nature, the yields, and the D content of the radiolytic products were determined by GLC-MS, using a 50-m-long, 0.20-mm-i.d. fused-silica column, coated with a 0.5- $\mu$ m crosslinked methylsilicone film (Hewlett-Packard PONA column), mounted on a HP 5890 gas chromatograph in series with a HP mass selective detector model 5970B. The isotopic content of the *tert*-butylated and trimethylsilylated products was deduced from the ratio of the abundancies of the corresponding [M - 15]<sup>+</sup> ions, the base peaks in their EI mass spectra. Formation of these ions involves direct cleavage of a methyl radical from the Me<sub>3</sub>C(Si) group in the molecular ion, with no scrambling of hydrogens from the aromatic ring, as checked from suitably labeled compounds.

## Results

Table I illustrates the *tert*-butylation and trimethylsilylation of *o*-, *m*-, and *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>D (*o*-D, *m*-D, and *p*-D) by Me<sub>3</sub>X<sup>+</sup> ions (X = C or Si) at ca. 1 atm. Both reactions are well characterized ionic reactions whose absolute radiochemical yields (*G* values) undergo the expected decrease upon addition of bases/nucleophiles, which intercept the reactant cations and/or their ionic precursors. Absolute yields are not affected by the presence of 10 Torr of O<sub>2</sub>, an effective radical scavenger. The radiolytic reactions are typically run to less than 1% conversion of the starting substrate, which means that the substrate concentration and that of any additive comparable to it are effectively constant during the time lapse of the experiment. The *tert*-butylation reaction is the one most thoroughly investigated, at three different temperatures in the case of *p*-D and in the presence of varying amounts of pyridine, a base whose proton affinity (PA = 221 kcal mol<sup>-1</sup>)<sup>8</sup> enables fast deprotonation of alkylated arenium ions. As previously reported,<sup>4</sup> only the meta and para isomers are formed. For each isomer, the percentages of deuterated and unlabeled products are reported in Table I after correction for the incomplete deuteration of the substrate (i.e., they refer to a hypothetical 100% monodeuterated toluene substrate, under the assumption that the residual un-

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Table I. Gas-Phase Reaction of  $\text{Me}_3\text{X}^+$  Ions ( $\text{X} = \text{C}$  or  $\text{Si}$ ) with *o*-, *m*-, and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{D}$  (*o*-D, *m*-D, and *p*-D)

system composition (Torr) <sup>a</sup>				temp (°C)	reactant ion: $\text{Me}_3\text{X}^+$	products: $\text{Me}_3\text{X}$ -substituted toluenes			
toluene	pyridine	bulk gas	isomeric composition (%)			H(D) content in each isomer <sup>b</sup> (%)			
			meta			para	meta	para	
p-D, 1.8		695	47	X = C	20	80	23 (77)	45 (55)	
p-D, 1.7	1.2	690	47	X = C	8	92	27 (73)	82 (18)	
p-D, 2.1	1.5	685	47	X = C	9	91	27 (73)	84 (16)	
p-D, 1.8	2.4	680	47	X = C	7	93	27 (73)	87 (13)	
p-D, 1.6	3.3	695	47	X = C	8	92	26 (74)	90 (10)	
p-D, 2.0	4.7	690	47	X = C	4	96	27 (73)	92 (8)	
p-D, 1.7	7.3	695	47	X = C	5	95	26 (74)	95 (5)	
p-D, 0.9	0.8	680	80	X = C	37	63	25 (75)	60 (40)	
p-D, 1.7	2.2	680	80	X = C	28	72	25 (75)	71 (29)	
p-D, 1.5	3.8	710	80	X = C	22	78	24 (76)	78 (22)	
p-D, 1.2	5.6	690	80	X = C	19	81	25 (75)	81 (19)	
p-D, 1.0	1.1	680	120	X = C	51	49	25 (75)	53 (47)	
p-D, 1.3	2.1	700	120	X = C	40	60	25 (75)	64 (36)	
p-D, 1.3	3.9	690	120	X = C	39	61	26 (74)	66 (34)	
p-D, 1.7	6.1	690	120	X = C	35	65	26 (74)	71 (29)	
m-D, 1.6	1.2	700	47	X = C	9	91	28 (72)	15 (85)	
m-D, 1.2	1.9	700	47	X = C	8	92	27 (73)	13 (87)	
m-D, 1.5	3.1	700	47	X = C	6	94	30 (70)	13 (87)	
m-D, 1.8	4.0	700	47	X = C	6	94	30 (70)	12 (88)	
m-D, 1.7	7.3	710	47	X = C	7	93	28 (72)	10 (90)	
o-D, 2.4		685	47	X = C	12	88	21 (79)	11 (89)	
o-D, 2.3	1.0	680	47	X = C	10	90	12 (88)	4 (96)	
o-D, 2.3	3.2	690	47	X = C	6	94	10 (90)	3 (97)	
o-D, 2.3	4.6	690	47	X = C	5	95	12 (88)	1 (99)	
o-D, 1.6	3.9	700	120	X = C	28	72	12 (88)	3 (97)	
o-D, 1.2	7.0	680	120	X = C	25	75	12 (88)	1 (99)	
p-D, 1.4	1.3 <sup>c</sup>	680	47	X = Si	17	83	0 (100)	98 (2)	
m-D, 0.9	0.8 <sup>c</sup>	710	47	X = Si	20	80	40 (60)	0 (100)	

<sup>a</sup> The gaseous systems contained  $\text{O}_2$  (10 Torr). The bulk gas was *i*- $\text{C}_4\text{H}_{10}$  ( $\text{X} = \text{C}$ ) or a 35/1 mixture of  $\text{CH}_4$ -( $\text{CH}_3$ )<sub>3</sub>Si ( $\text{X} = \text{Si}$ ). <sup>b</sup> The deuterium content in each isomer has been normalized with respect to a hypothetical 100% deuterated substrate, considering that the % fraction of undeuterated substrate would give an equal % fraction of undeuterated products. Standard deviation of data:  $\pm 2\%$ . <sup>c</sup> Triethylamine has been used instead of pyridine.

deuterated toluene contributes to the formation of the unlabeled product proportionally to its mole fraction). In the case of *m*-*tert*-butyltoluene, irrespective of the position of the label, the results obtained in the presence of pyridine are invariant with respect to changes in the temperature and the base concentration. On the other hand, the D content of the *p*-*tert*-butyltoluene from the reaction of *p*-D decreases markedly at higher pyridine concentrations. A less pronounced, but still significant increase of the D content is found in *p*-*tert*-butyltoluene from the reaction of *m*-D, while nearly constant values, close to 100% D retention, are found in the product from the reaction of *o*-D in the presence of pyridine. The D content of *p*-*tert*-butyltoluene from *p*-D is higher at higher temperatures, reaching 47% at 120 °C in the presence of 1.1 Torr of pyridine.

The competitive *tert*-butylation of  $\text{C}_6\text{H}_6$ - $\text{C}_6\text{D}_6$  and  $\text{CH}_3\text{C}_6\text{H}_5$ - $\text{CD}_3\text{C}_6\text{D}_5$  mixtures is illustrated in Table II. The relative yields of deuterated and unlabeled products normalized by the molar ratio of the respective substrates give the overall  $k_{\text{H}}/k_{\text{D}}$  values. In the case of benzene, a remarkably constant  $k_{\text{H}}/k_{\text{D}}$  ratio of  $2.0 \pm 0.1$  was observed, unaffected by a temperature change from 47 °C to 120 °C and by variable concentrations of bases of different strength from 1,4-dioxane ( $\text{PA} = 194 \text{ kcal mol}^{-1}$ ) to piperidine ( $\text{PA} = 226 \text{ kcal mol}^{-1}$ )<sup>8</sup>. The *tert*-butylation of toluene showed lower  $k_{\text{H}}/k_{\text{D}}$  ratios which, in the case of *p*-*tert*-butyltoluene, decreased on addition of pyridine. The presence of pyridine proved almost ineffective in the case of *m*-*tert*-butyltoluene. Increasing the temperature from 47 to 120 °C resulted in somewhat higher  $k_{\text{H}}/k_{\text{D}}$  ratios.

The isomeric composition of *tert*-butyltoluenes shows the previously reported<sup>4</sup> dependence on the temperature and the base concentration (Tables I and II). Higher temperatures and the absence of strong bases favor the formation of the meta isomer, which under otherwise equal conditions, also seems favored by a higher toluene concentration.

The last entries in Table I refer to trimethylsilylation, which differs markedly from *tert*-butylation. Thus, the reaction of

$\text{Me}_3\text{Si}^+$  ions with *p*-D yields *p*- $\text{Me}_3\text{Si}$ -substituted toluene with total loss of deuterium, which is instead completely retained in the *m*- $\text{Me}_3\text{Si}$ -substituted toluene formed. Complete retention of D is also observed in *p*- $\text{Me}_3\text{Si}$ -substituted toluene from *m*-D. As shown in Table II, trimethylsilylation of  $\text{C}_6\text{H}_6$ - $\text{C}_6\text{D}_6$  mixtures gives an apparent  $k_{\text{H}}/k_{\text{D}}$  ratio of 1.1 in the presence of 0.83 Torr of  $\text{NET}_3$ , a powerful, hindered base ( $\text{PA} = 232 \text{ kcal mol}^{-1}$ )<sup>8</sup>. A few attempts to perform the reaction in the presence of weaker nitrogen bases, e.g.,  $\text{C}_2\text{H}_5\text{CN}$  and  $(\text{CF}_3)_3\text{CNH}_2$ , failed to yield  $\text{Me}_3\text{SiPh}$ , formation of which is known to require intervention of a strong nitrogen base.<sup>9</sup>

## Discussion

**H-Shifts upon  $\text{Me}_3\text{C}^+$  Attack on Toluene.** It is generally recognized that conventional aromatic substitution by a  $\text{E}^+$  electrophile involves intermediacy of a  $\sigma$  complex whereby the E group and a H atom are geminally bound to a  $\text{sp}^3$  carbon. The *p*-*tert*-butylation of *p*-D by gaseous  $\text{Me}_3\text{C}^+$  ions has provided direct evidence for the formation in the gas phase of such complexes (II in Scheme II, an appropriately rewritten Scheme I), trapped by deuterium transfer to pyridine (P). At relatively high pyridine concentrations, some 95% of *p*-*tert*-butyltoluene formed at 47 °C has lost the label initially present in the substrate. At lower pyridine concentrations the *p*-*tert*-butyltoluene formed retains increasingly higher amounts of D, which, referring to Scheme II, is explained by the increasing fraction of ions II undergoing isomerization to III by D shift to the position ortho to the *tert*-butyl group, as allowed by their longer lifetimes before deprotonation. Ions III can be neutralized by the base or, in turn, undergo further isomerization by proton shifts. The reaction of *o*-D provides an indication of the progress of H/D shifts to ring positions farther from the initial site of the  $\text{Me}_3\text{C}^+$  attack. Significant formation

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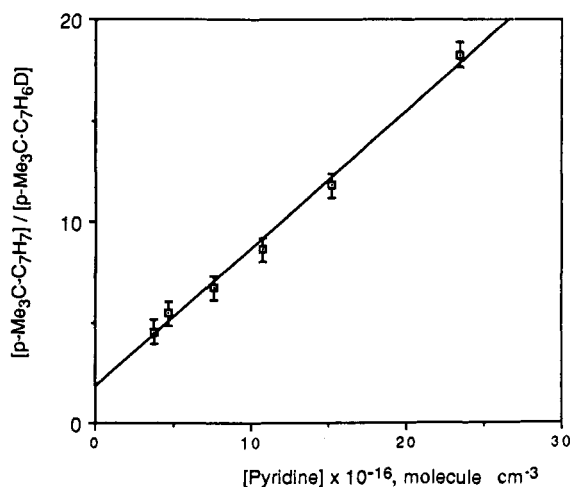
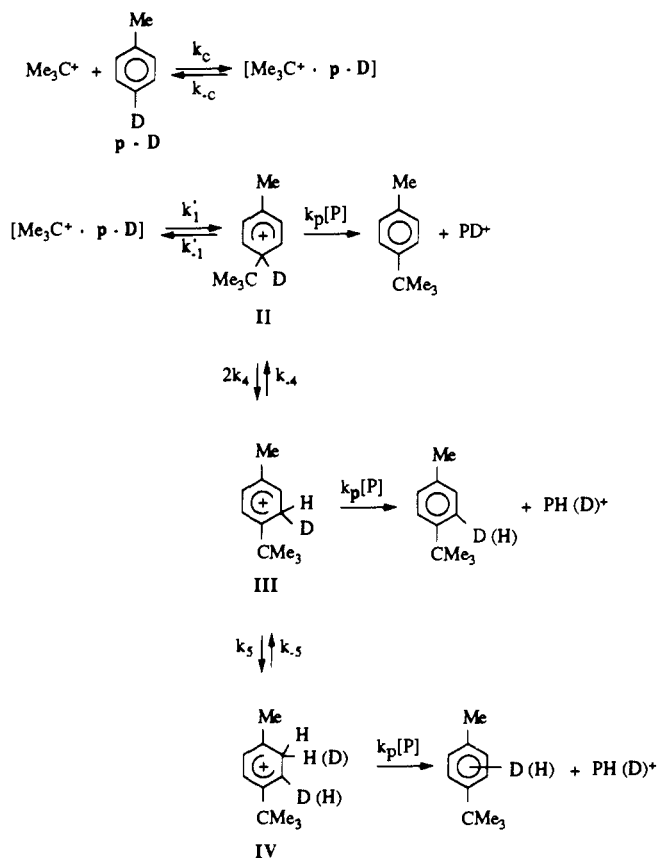


Figure 1. Dependence of the undeuterated to deuterated *p-tert*-butyltoluene product ratio from the reaction of gaseous  $\text{Me}_3\text{C}^+$  ions with *p*- $\text{MeC}_6\text{H}_4\text{D}$ , at 47 °C, on the concentration of added pyridine.

## Scheme II



of IV in Scheme II should lead to depletion of the D content in the *p-tert*-butyltoluene formed from o-D. Actually, the decrease of the D content shown in Table I for the *p-tert*-butylation of o-D in the presence of varying amounts of pyridine is barely above the error span both at 47 °C and at 120 °C, which can be taken as an indication that formation of IV is negligible under the experimental conditions explored, i.e., at pyridine partial pressures >1 Torr. With this simplification, the ratio of unlabeled to deuterated products can be analyzed applying to kinetic Scheme II the conventional steady-state treatment, which predicts a linear dependence of the above ratio on the pyridine concentration

$$\frac{[p\text{-Me}_3\text{CC}_7\text{H}_7]}{[p\text{-Me}_3\text{CC}_7\text{H}_6\text{D}]} = \frac{2(k_{-4} + k_p[\text{P}])}{k_4} + 1 \quad (4)$$

This expectation is borne out, as shown by the plot illustrated in

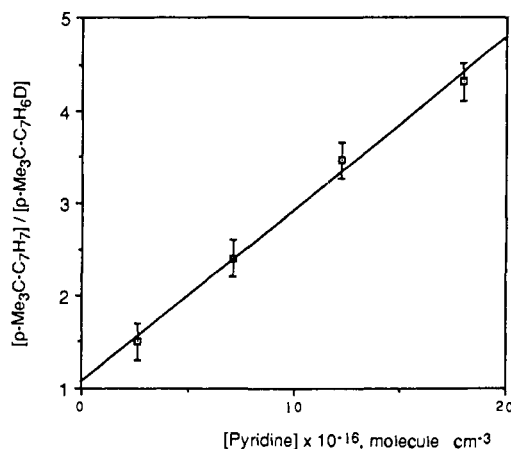


Figure 2. Dependence of the undeuterated to deuterated *p-tert*-butyltoluene product ratio from the reaction of gaseous  $\text{Me}_3\text{C}^+$  ions with *p*- $\text{MeC}_6\text{H}_4\text{D}$ , at 80 °C, on the concentration of added pyridine.

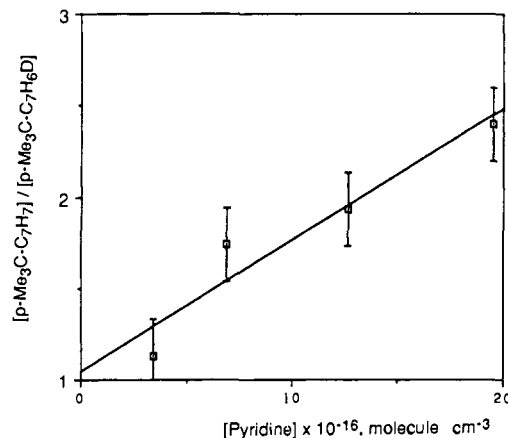


Figure 3. Dependence of the undeuterated to deuterated *p-tert*-butyltoluene product ratio from the reaction of gaseous  $\text{Me}_3\text{C}^+$  ions with *p*- $\text{MeC}_6\text{H}_4\text{D}$ , at 120 °C, on the concentration of added pyridine.

Figure 1, which obeys a fairly linear relationship, confirming that formation of IV can legitimately be neglected, since if significant, it should lead to a curvilinear plot. Similar plots are obtained at 47 °C (Figure 1), 80 °C (Figure 2), and 120 °C (Figure 3), all showing an intercept close to 1, suggestive of  $2k_{-4} \ll k_4$ . The slopes, equal to  $2k_p/k_4$ , allow one to evaluate  $k_4$  (Table III), by assuming that deprotonation by pyridine occurs at the collision frequency, which can be calculated by the ADO theory.<sup>10</sup> In doing so, it is assumed that the  $k_p$  process is not affected by any primary KIE, which is reasonable in view of the large basicity difference between the *tert*-butylated arene ( $\text{PA} < 204 \text{ kcal mol}^{-1}$ )<sup>8</sup> and pyridine ( $\text{PA} = 221 \text{ kcal mol}^{-1}$ ).<sup>8</sup> The corresponding  $\text{p}K_a$  difference, larger than 12 units at 25 °C, places the deprotonation process rather far from the  $\Delta\text{p}K_a = 0$  condition, predicted to lead to the maximum primary KIE according to the Bell criterion.<sup>11,12</sup>

(10) Bowers, M. T.; Su, T. In *Interactions between Ions and Molecules*; Ausloos, P., Ed.; Plenum Press: New York, 1975; p 163. The strong thermodynamic drive for proton transfer between I ( $\text{E} = \text{Me}_3\text{C}$ ,  $\text{R} = \text{H}$ ,  $\text{Me}$ ) and pyridine ( $\Delta\text{PA} > 20 \text{ kcal mol}^{-1}$ ) ensures a greater than 80% reaction efficiency, i.e.,  $k_p > 0.8 k_{\text{ADO}}$ . In those cases where the reaction is nearly thermoneutral, the efficiency can be lower, cf. Bükér, H.; Grützmaier, H.-F. *Int. J. Mass Spectrom. Ion Processes* 1991, 109, 95.

(11) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980.

(12) Unfortunately, few kinetic isotope effects have been reported in gas-phase ion-molecule reactions, and no general trends are available to test the validity of the Bell criterion in proton-transfer reactions between gaseous species. (a) Gronert, S.; De Puy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* 1991, 113, 4009. (b) Bierbaum, V. M.; Filley, J.; De Puy, C. H.; Jarrold, M. F.; Bowers, M. T. *J. Am. Chem. Soc.* 1985, 107, 2818. (c) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* 1987, 109, 1715. (d) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* 1980, 102, 2906. (e) Wellman, K. M.; Victoriano, M. E.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* 1979, 101, 2242.

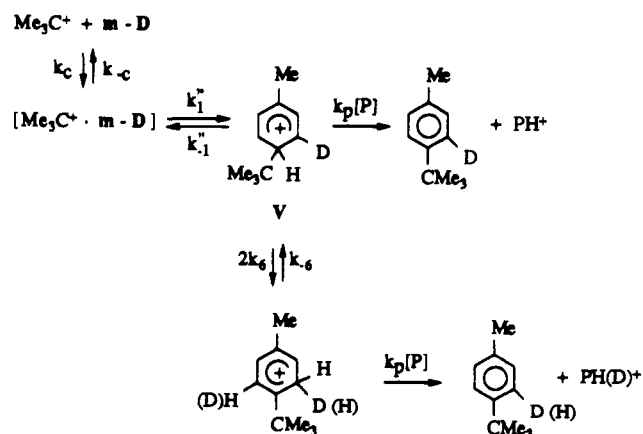
**Table II.** Gas-Phase Reaction of  $\text{Me}_3\text{X}^+$  Ions ( $\text{X} = \text{C}$  or  $\text{Si}$ ) with  $\text{C}_6\text{H}_6$ - $\text{C}_6\text{D}_6$  and  $\text{C}_6\text{H}_5$  CH- $\text{C}_6\text{D}_5\text{CD}_3$  Mixtures

system composition (Torr) <sup>a</sup>			temp (°C)	reactant ion: $\text{Me}_3\text{X}^+$	isomeric composition of <i>tert</i> -butyltoluenes (%)		$k_{\text{H}}/k_{\text{D}}$
substrates	additive	bulk gas			meta	para	
$\text{C}_6\text{H}_6$ , 1.4 $\text{C}_6\text{D}_6$ , 1.4		650	47	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 1.6 $\text{C}_6\text{D}_6$ , 2.0	1,4-dioxane, 2.4	660	47	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 1.8 $\text{C}_6\text{D}_6$ , 1.7	EtNO <sub>2</sub> , 1.2	690	47	$\text{X} = \text{C}$			2.0
$\text{C}_6\text{H}_6$ , 1.3 $\text{C}_6\text{D}_6$ , 1.1	pyridine, 0.74	690	47	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 1.5 $\text{C}_6\text{D}_6$ , 1.2	pyridine, 1.2	690	47	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 2.1 $\text{C}_6\text{D}_6$ , 2.0	piperidine, 1.3	650	47	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 2.5 $\text{C}_6\text{D}_6$ , 2.2		650	120	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 1.3 $\text{C}_6\text{D}_6$ , 1.3	1,4-dioxane, 2.9	690	120	$\text{X} = \text{C}$			2.0
$\text{C}_6\text{H}_6$ , 1.4 $\text{C}_6\text{D}_6$ , 1.5	EtNO <sub>2</sub> , 3.4	690	120	$\text{X} = \text{C}$			2.0
$\text{C}_6\text{H}_6$ , 2.2 $\text{C}_6\text{D}_6$ , 1.6	(MeO) <sub>2</sub> CO, 1.8	630	120	$\text{X} = \text{C}$			2.0
$\text{C}_6\text{H}_6$ , 0.9 $\text{C}_6\text{D}_6$ , 0.8	pyridine, 2.0	700	120	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 1.0 $\text{C}_6\text{D}_6$ , 1.2	pyridine, 3.9	690	120	$\text{X} = \text{C}$			2.0
$\text{C}_6\text{H}_6$ , 1.7 $\text{C}_6\text{D}_6$ , 1.5	piperidine, 3.9	690	120	$\text{X} = \text{C}$			2.1
$\text{C}_6\text{H}_6$ , 1.1 $\text{C}_6\text{D}_6$ , 1.5	NEt <sub>3</sub> , 0.83	700	47	$\text{X} = \text{Si}$			1.1
$\text{C}_7\text{H}_8$ , 2.0 $\text{C}_7\text{D}_8$ , 2.1		650	47	$\text{X} = \text{C}$	12	88	meta: 1.0 para: 1.3
$\text{C}_7\text{H}_8$ , 2.0 $\text{C}_7\text{D}_8$ , 2.0	pyridine, 4.4	690	47	$\text{X} = \text{C}$	15	85	meta: 1.0 para: 1.0
$\text{C}_7\text{H}_8$ , 1.8 $\text{C}_7\text{D}_8$ , 2.0		690	120	$\text{X} = \text{C}$	8	92	meta: 1.0 para: 1.0
$\text{C}_7\text{H}_8$ , 2.0 $\text{C}_7\text{D}_8$ , 2.0		690	120	$\text{X} = \text{C}$	7	93	meta: 1.5 para: 1.6
$\text{C}_7\text{H}_8$ , 2.3 $\text{C}_7\text{D}_8$ , 2.0	pyridine, 5.1	700	120	$\text{X} = \text{C}$	53	47	meta: 1.5 para: 1.3
$\text{C}_7\text{H}_8$ , 0.15 $\text{C}_7\text{D}_8$ , 0.14	pyridine, 4.5	700	120	$\text{X} = \text{C}$	55	45	meta: 1.5 para: 1.3
					24	76	meta: 1.5 para: 1.3
					21	79	meta: 1.5 para: 1.3
					18	82	meta: 1.5 para: 1.3

<sup>a</sup> See footnote a in Table I.**Table III.** Kinetic Data on H(D) Shifts within *tert*-Butylarenium Ions

process	temp (°C)	kinetic data
	47 80 120	$k_4 = 5.2 \pm 0.2 \times 10^7 \text{ s}^{-1}$ $k_4 = 1.9 \pm 0.1 \times 10^8 \text{ s}^{-1}$ $k_4 = 4.7 \pm 0.1 \times 10^8 \text{ s}^{-1}$
	47	$k_6 = 4.4 \pm 2.3 \times 10^8 \text{ s}^{-1}$
	47 80 120	$k_7/k_8 = 0.85 \pm 0.13$ $k_7, k_8 \gg 8.5 \times 10^8 \text{ s}^{-1}$ $k_7/k_8 = 1.0 \pm 0.2$ $k_7/k_8 = 1.0 \pm 0.15$

Whereas the  $k_4$  value obtained from the *p*-*tert*-butylation reaction of *p*-D refers to a D shift, a similar treatment of the results concerning the D content in *p*-*tert*-butyltoluene from *m*-D yields information on the same process involving a H shift (Scheme III). In this case, increasing [P] leads to an increased [*p*-

**Scheme III**

$\text{Me}_3\text{CC}_7\text{H}_6\text{D}] / [p\text{-Me}_3\text{CC}_7\text{H}_7]$  ratio, whose dependence on the concentration of pyridine plotted in Figure 4 is described by eq 5. Unfortunately, the value of  $k_6 = 4.4 \pm 2.3 \times 10^8 \text{ s}^{-1}$ , derived

$$\frac{[p\text{-Me}_3\text{CC}_7\text{H}_6\text{D}]}{[p\text{-Me}_3\text{CC}_7\text{H}_7]} = 2 \frac{k_p[\text{P}]}{k_6} + 3 \quad (5)$$

by assuming an equal rate of H migration to the adjacent H- and D-bearing carbons, is appreciably affected by the uncertainty of the D content data. Nevertheless, a distinct KIE on the 1,2-H migration process considered is clearly discernible even from such an approximate estimate.

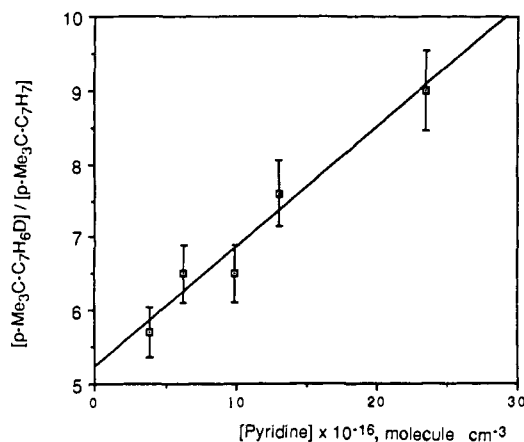


Figure 4. Dependence of the deuterated to undeuterated *p*-*tert*-butyltoluene product ratio from the reaction of gaseous  $\text{Me}_3\text{C}^+$  ions with *m*- $\text{MeC}_6\text{H}_4\text{D}$ , at 47 °C, on the concentration of added pyridine.

The reactivity pattern that emerges from the above considerations shows that the attack of  $\text{Me}_3\text{C}^+$  ions at the para position of toluene leading to II/V is followed by a relatively slow H/D migration to the adjacent position, a process occurring on the nanosecond time frame of the reactive collisions with the base. Since the concentration of the latter is less than 1 mol %, it follows that the ions II/V have undergone several tens of unreactive collisions with the bulk gas, disposing of any excess internal energy derived from their formation process *before* the shift can occur. Thus, it can be asserted that *the observed H/D shifts take place in a gaseous ion in a truly thermal equilibrium with the bath gas*, a condition not always attainable, not even in the relatively high-pressure range accessible to the radiolytic technique.

A very different situation is delineated by the data concerning the formation of *m*-*tert*-butyltoluene. The D content in this product is insensitive to the concentration of the base, yet it is markedly lower than in the starting substrates, i.e., *o*-D, *m*-D, or *p*-D. This behavior suggests that the 1,2-H(D) shift from the position attacked by  $\text{Me}_3\text{C}^+$  is too fast to be intercepted by collisions with the base. Within the framework of Scheme IV, which shows *p*-D as the substrate, the  $k_7$  and  $k_8$  rate constants must be much larger than  $k_p[\text{P}]$  even at the highest concentration of pyridine used, when  $k_p[\text{P}] \approx 8.5 \times 10^8 \text{ s}^{-1}$ .

From the fraction of deuterium in the *m*-*tert*-butyltoluene formed from *p*-D under various conditions one derives  $k_7/k_8$  ratios close to unity, whose values are reported in Table III, based again on the neglect of any KIE on the deprotonation of the *tert*-butylarenium ions by pyridine. The arenium ions VI and VII are highly stabilized by two alkyl groups in ortho/para positions, which accounts for the omission of  $k_{-7}$  and  $k_{-8}$  from Scheme IV.

**Activation Parameters for 1,2-H(D) Shifts.** The  $k_4$  values at three different temperatures reported in Table III have been used for the construction of the Arrhenius plot shown in Figure 5, which contains only three points. Despite this obvious limitation, the plot is fairly linear over the rather extended temperature range investigated. The derived  $E_a = 7.6 \pm 0.2 \text{ kcal mol}^{-1}$  and  $\log A = 12.9 \pm 0.4$  represent the first independent estimates of the activation parameters for a *thermal* 1,2-H(D) migration process within a gaseous arenium ion, and hence can legitimately be compared to the values,  $E_a = 10 \pm 1 \text{ kcal mol}^{-1}$  and  $\log A = 15.9 \pm 1.6$ , for 1,2-H shifts in benzenium ions, the model system studied by Olah et al. in superacids.<sup>13</sup> Though the gaseous and the superacid media are very different, the two systems bear a similarity in that H shifts are in both cases thermoneutral processes, as shown in the following section, and hence the observed similarity of the Arrhenius activation energies is not entirely fortuitous. As a matter of fact, the few available data on the *thermal* proton shifts in gaseous arenium ions<sup>8a,7b</sup> point to activation barriers of the order of 10 kcal mol<sup>-1</sup>, and provide no evidence for the free

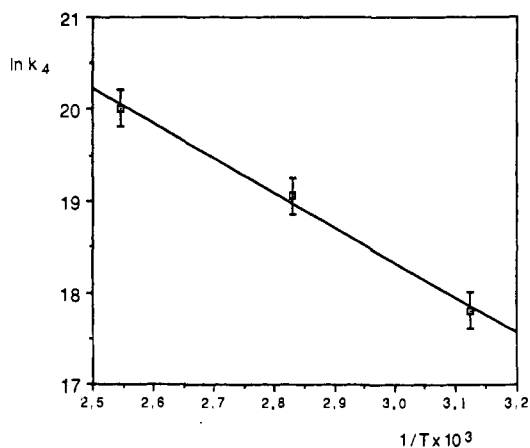
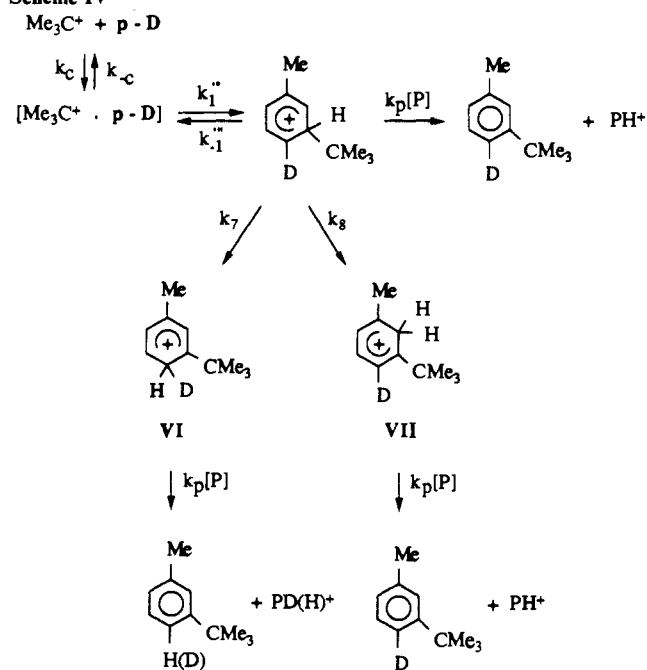


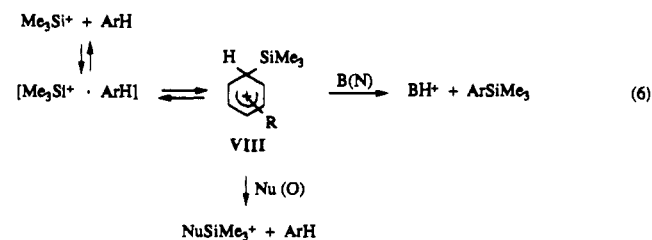
Figure 5. Arrhenius plot showing the temperature dependence of the  $k_4$  rate constant. Plotted data are from Table III.

#### Scheme IV



proton motion postulated to occur in gaseous arenium ions to account for certain anomalous thermochemical results.<sup>7d,14</sup>

**Kinetic Comparison with Trimethylsilylation.** The reaction of  $\text{Me}_3\text{Si}^+$  with arenes allows an interesting comparison with the *tert*-butylation reaction. The binding energies of  $\text{Me}_3\text{Si}^+$  to arenes, determined by pulsed high-pressure mass spectrometry, are similar to those of  $\text{Me}_3\text{C}^+$  ions.<sup>6,15</sup> It is now agreed that  $\sigma$ -complex intermediates are formed,<sup>6,9</sup> whose reactivity is strongly suggestive of a species bearing H and  $\text{Me}_3\text{Si}$  as geminal substituents at the tetrahedral carbon, e.g., VIII in reaction 6. In particular, arenium

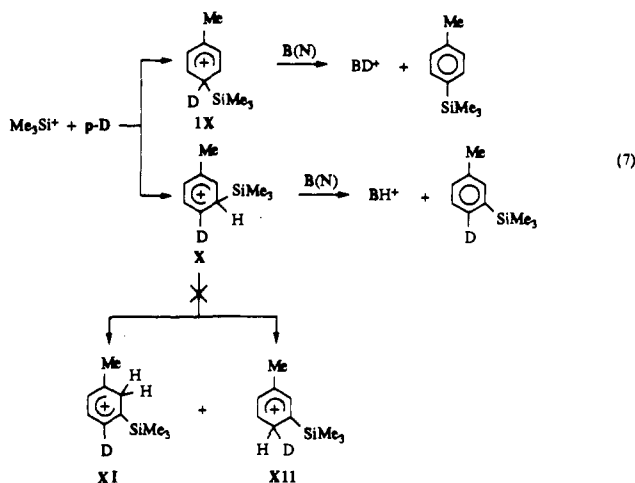


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ions VIII undergo competitive deprotonation and desilylation reactions. Strong nitrogen bases favor deprotonation, leading to silylated products, whereas oxygen nucleophiles, forming a strong Si-O bond, selectively remove the trimethylsilyl group.<sup>9</sup> Additional evidence for the kinetic role of VIII comes from the ease of cleavage of the Me<sub>3</sub>Si group, following protonation or alkylation of trimethylsilylbenzene and trimethylsilyltoluenes.<sup>7b,16</sup> Such a reactivity pattern has been accounted for by the enhanced basicity of the trimethylsilylated position of the aromatic ring, that is, by the comparatively high thermodynamic stability of species like VIII. Conclusive evidence for the scarce tendency of the ipso H in VIII to migrate to adjacent ring positions is provided by this work. The reaction of toluene with the Me<sub>3</sub>Si<sup>+</sup>, obtained from the reaction of the CH<sub>3</sub><sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup> ions from the ionization of methane with Me<sub>3</sub>Si,<sup>9,15</sup> is known to yield a 15/85 mixture of *m*- and *p*-trimethylsilyltoluenes.<sup>9</sup> The reactions of Me<sub>3</sub>Si<sup>+</sup> reported at the end of Table I show nearly complete loss of D in the para isomer and complete retention in the meta isomer from *p*-D, and in the para isomer from *m*-D, providing compelling evidence that no H/D shifts have indeed taken place from the silylated carbon. Such a finding is particularly significant in the case of the meta isomer. In fact, whereas the Me<sub>3</sub>Si<sup>+</sup> attack at the para position of toluene yields an arenium ion stabilized by a *p*-methyl and by an ipso trimethylsilyl group, the Me<sub>3</sub>Si<sup>+</sup> attack at the meta position yields an ion where the methyl group should rather favor migration of hydrogen to the adjacent positions.



The effect exerted by the ipso Me<sub>3</sub>Si substituent appears to be overwhelming in stabilizing species like IX and X in eq 7, even with respect to XI and XII. The possibility that the observed reluctance to H migration from the ipso-silylated position depends on kinetic, rather than thermodynamic factors, is not supported by the "normal" rates and activation energies recently reported for H shift within arenium ions bearing alkyl and trimethylsilyl substituents.<sup>7b</sup>

**Competitive *tert*-Butylation of C<sub>6</sub>H<sub>6</sub>-C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>-C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> Mixtures.** The previous discussion on the rates of H/D shifts upon Me<sub>3</sub>C<sup>+</sup> attack on toluene suggests the possibility that such processes are not necessarily fast. To inquire as to whether, and to what extent, the H migration step, e.g., *k*<sub>2</sub> in Scheme I, determines the overall *tert*-butylation rate, the relative reactivities of the C<sub>6</sub>H<sub>6</sub>/C<sub>6</sub>D<sub>6</sub> and the C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>/C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> pairs have been examined with the expectation that, should any H shift occur in a kinetically significant step of the reaction, this could result in a sizeable KIE. The data listed in Table II show that this indeed is the case. The C<sub>6</sub>H<sub>6</sub>/C<sub>6</sub>D<sub>6</sub> competition yields an overall *k*<sub>H</sub>/*k*<sub>D</sub> ratio of 2.0 ± 0.1, practically constant both at 47 °C and 120 °C, unaffected by addition of bases of varying strength from piperidine (PA = 226.4 kcal mol<sup>-1</sup>)<sup>8</sup> to nitroethane (PA = 184.8 kcal mol<sup>-1</sup>)<sup>8</sup>, chosen for its PA close to the value of 182.4 kcal mol<sup>-1</sup> calculated for the ipso position of *tert*-butylbenzene.<sup>16</sup>

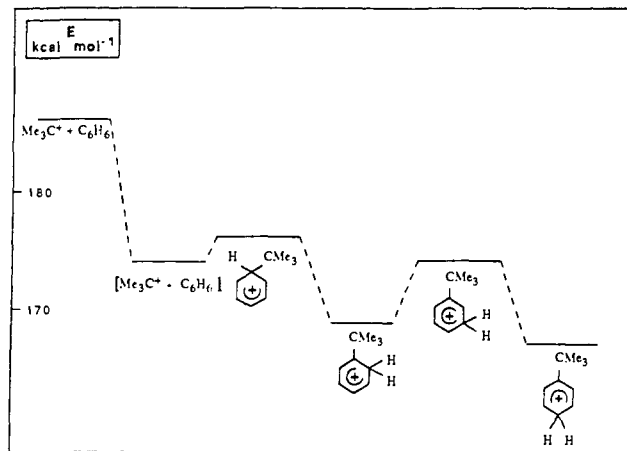


Figure 6. Energy profile for the Me<sub>3</sub>C<sup>+</sup> + C<sub>6</sub>H<sub>6</sub> system. The Δ*H*<sub>f</sub> of 4-*tert*-butylbenzenium ion has been obtained from the PA of *tert*-butylbenzene.<sup>8</sup> The relative stability of the other isomers has been estimated, assuming that the basicity differences calculated for the toluene ring positions hold also in the case of *tert*-butylbenzene.<sup>21</sup> It is to be reminded that the *tert*-butylation reaction is affected by a strongly unfavorable entropic term<sup>5,6</sup> which does not appear in the energy diagram. The binding energy of the [Me<sub>3</sub>C<sup>+</sup>·C<sub>6</sub>H<sub>6</sub>] collision complex has been assumed equal to that reported for the [Me<sub>2</sub>Cl<sup>+</sup>·PhMe] complex.

Referring to Scheme I, the collisional encounter *k*<sub>c</sub> step is not rate determining, as shown by the high substrate selectivity of Me<sub>3</sub>C<sup>+</sup> ions<sup>4</sup> and can be viewed as a rapid preequilibrium, whose *K*<sub>c</sub> constant is largely independent of isotopic substitution in the arene. The *k*<sub>1</sub> rate constant of the electrophilic attack could conceivably include a small *inverse* KIE, due to the sp<sup>2</sup> → sp<sup>3</sup> hybridization change of the H(D)-bearing carbon, site of reaction, and possibly to a secondary KIE. The mildly activating polar effect of D versus H should be negligible, at least it seems not to affect proton-transfer equilibria of methylbenzenes<sup>17</sup> nor the binding energies of Me<sub>3</sub>C<sup>+</sup> to C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>.<sup>6</sup> A net H motion comes into play only when considering the deprotonation and the proton-shift steps. Under the simplifying assumption that *k*<sub>-2</sub> and *k*<sub>3</sub>, which in this case (R = H) concern processes leading to thermodynamically less stable ions as shown by the energy profile in Figure 6, are much smaller than *k*<sub>B</sub>[B], the overall rate constant is approximated by the expression

$$k_{\text{overall}} = K_c \frac{k_1(k_2 + k_B[B])}{k_{-1} + k_2 + k_B[B]} \quad (8)$$

The observation that the *k*<sub>H</sub>/*k*<sub>D</sub> is insensitive to changes in the strength and the concentration of the base provides strong evidence that *k*<sub>2</sub> is much larger than *k*<sub>B</sub>[B], which leads to the simplified expression

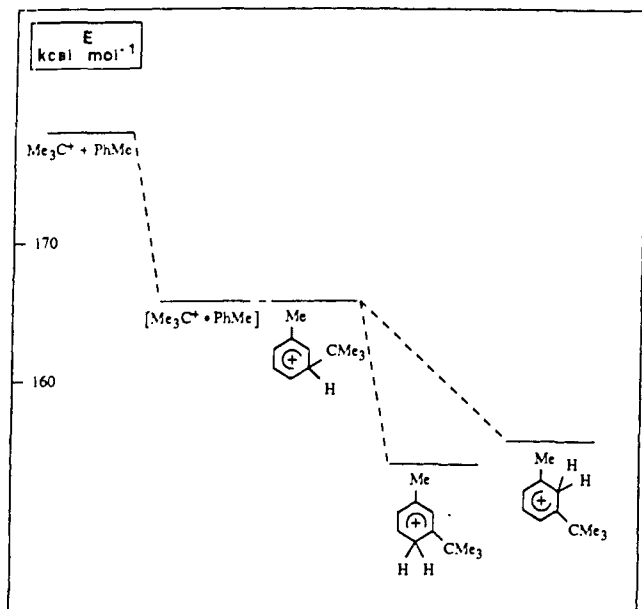
$$k_{\text{overall}} = K_c \frac{k_1 k_2}{k_{-1} + k_2} \quad (9)$$

Since the dependence of *k*<sub>1</sub> and *k*<sub>-1</sub> on the isotopic substitution is due only to secondary effects, the observed *k*<sub>H</sub>/*k*<sub>D</sub> should be determined mainly by the *k*<sub>2</sub>(H)/*k*<sub>2</sub>(D) ratio and by the relative magnitudes of *k*<sub>-1</sub> and *k*<sub>2</sub>. Both factors should show a temperature dependence. In most common cases,<sup>18</sup> primary KIEs show a negative temperature dependence, i.e., *k*<sub>2</sub>(H)/*k*<sub>2</sub>(D) is expected to decrease at higher temperatures, whereas *k*<sub>-1</sub>/*k*<sub>2</sub> should increase, since the entropically favored back dissociation should be enhanced at higher temperatures, leading to larger *k*<sub>H</sub>/*k*<sub>D</sub> values. Thus, the observed invariance of *k*<sub>H</sub>/*k*<sub>D</sub> at widely different temperatures could reflect a fortuitous balance of the two effects. According to eq 9, the observed *k*<sub>H</sub>/*k*<sub>D</sub> represents only a lower limit to *k*<sub>2</sub>(H)/*k*<sub>2</sub>(D), which implies *k*<sub>2</sub>(H)/*k*<sub>2</sub>(D) >> 2. Such a lower limit for *k*<sub>2</sub>(H)/*k*<sub>2</sub>(D) (R = H) may be compared to the grossly ap-

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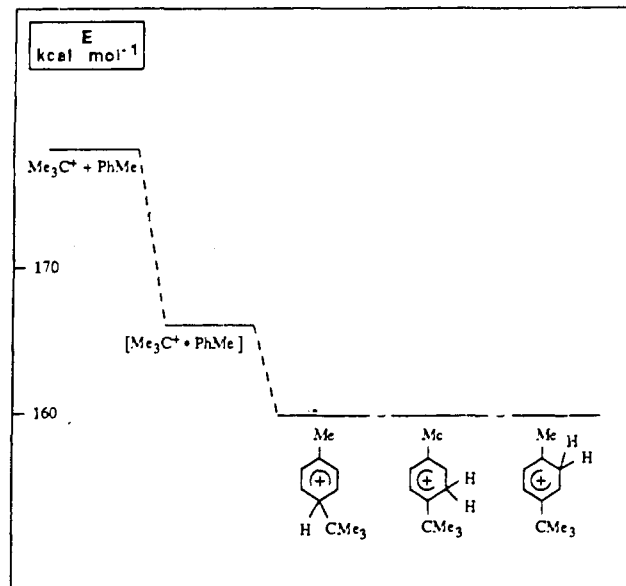
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**Figure 7.** Energy profile for the attack of  $\text{Me}_3\text{C}^+$  to the meta position of toluene. The stability of the isomeric protonated *m*- and *p*-*tert*-butyltoluenes has been estimated assuming the additivity of *tert*-butyl and methyl substituent effects.<sup>21</sup> The binding energy of the  $[\text{Me}_3\text{C}^+\cdot\text{PhMe}]$  collision complex has been taken equal to that of  $[\text{Me}_2\text{Cl}^+\cdot\text{PhMe}]$ .<sup>22</sup>

proximate  $k_2(\text{H})/k_2(\text{D}) = 8 \pm 4$  ( $\text{R} = p\text{-Me}$ ) derived from the data of Table III. Despite the large uncertainties affecting both sets of data, they concur in showing that a fairly large isotope effect may be attached to *thermal* 1,2-H shifts in arenium ions, and to our knowledge, they represent the first recognition of isotope effects in these processes. A related process is the aromatic hydrogen exchange in concentrated aqueous sulfuric acid, though it concerns intermolecular, rather than intramolecular proton transfer. Several data from different workers have been recently analyzed, showing relatively large isotope effects ( $k_{\text{H}}/k_{\text{D}} = \text{ca } 5.3 \pm 2.1$ ) for the deprotonation of arenium intermediates.<sup>19</sup> The 1,2-H shift taking place in the  $k_2$  step implies a bent transition state, and current semiclassical theories on primary isotope effects predict a reduction of its maximum value when a bending character of the reaction coordinate is involved.<sup>11</sup> However, two items should be considered. First, the observed isotope effect is not purely primary, but particularly as regards the competition of  $\text{C}_6\text{H}_6$  versus  $\text{C}_6\text{D}_6$ , the H/D substitution involves not only the reaction center and the migrating atom but also farther positions, whose vibrational frequencies will also change. Thus, even restricting the analysis to the elementary 1,2 migration step, this will include several contributions whose relative weight is not easily predictable. Second, the range of KIEs in gas-phase reactions can conceivably be different from that observed in condensed-phase reactions, where coupling between the proton motion and the environment can be strong, e.g., a relatively large KIE ( $k_{\text{H}}/k_{\text{D}} = 3.7$  at 300 K) has been calculated recently for the intramolecular proton transfer in isolated hydrogenoxalate anion.<sup>20</sup>

The insight into the timing of 1,2-H shifts following  $\text{Me}_3\text{C}^+$  ion attack on monodeuterated toluenes and the overall  $k_{\text{H}}/k_{\text{D}}$  ratios from the  $\text{C}_6\text{H}_5\text{CH}_3/\text{C}_6\text{D}_5\text{CD}_3$  competition concur in outlining a coherent picture of the detailed course of gas-phase *tert*-butylation of toluene. The attack at the para position gives an arenium ion stabilized by a *p*-methyl group, according to a process more exothermic than the corresponding reaction at the meta position of toluene or with benzene, as shown by the energy profiles in



**Figure 8.** Energy profile for the attack of  $\text{Me}_3\text{C}^+$  to the para position of toluene. See notes to Figure 7.

figures 7 and 8. It seems reasonable to argue that the ensuing arenium ion  $\text{I}_p$  ( $\text{I}_p = \text{I}$ ,  $\text{R} = p\text{-Me}$ ) will be less prone to back dissociation, i.e.,  $k_{-1}$  is smaller. Its fate will then be determined by the  $k_{\text{B}}[\text{B}]/k_2$  ratio, since neither  $k_{-2}$  nor  $k_3$  are significant, and eq 8 will hold. In agreement with these expectations  $k_{\text{H}}/k_{\text{D}}$  values are observed to *decrease* in the presence of pyridine, e.g.,  $k_{\text{H}}/k_{\text{D}}$  varies from 1.3 with no bases added to 1.0 in the presence of 4.4 Torr of pyridine at 47 °C. At 120 °C, the  $k_{\text{H}}/k_{\text{D}}$  ratios, still sensitive to the addition of pyridine, have somewhat higher values, traced to increased  $k_{-1}$ , whereas  $k_{\text{B}}$  undergoes the weak negative temperature effect typical of collisional rate constants.

The kinetic pattern that characterizes  $\text{Me}_3\text{C}^+$  attack at the meta position of toluene is quantitatively different from that pertaining to its attack at the para position. Changes in the base concentration were seen not to affect the fast H migration both at 47 °C and at 120 °C, and eq 9 then applies. Accordingly, the  $k_{\text{H}}/k_{\text{D}}$  ratios are unaffected by the presence of the base, and that the  $k_{\text{H}}/k_{\text{D}}$  ratio = 1.0 at 47 °C is indicative of  $k_2 \gg k_{-1}$  at that temperature, whereas the two constants must be comparable to 120 °C leading to  $k_{\text{H}}/k_{\text{D}} = 1.5$ . The  $\text{Me}_3\text{C}^+$  ion attacks on benzene or at the meta positions of toluene bear some similarity due to the lack of the activating effect of a *p*-methyl group, and their  $k_{-1}$  are probably close. Therefore, since eq 9 likely holds in both cases, their different  $k_{\text{H}}/k_{\text{D}}$  ratios point to a large difference in the  $k_2$  rate constants, either in absolute value and/or in isotopic sensitivity. It may be recalled that when  $\text{R} = m\text{-Me}$  the  $k_2$  step leads to arenium ions stabilized by *two* alkyl groups, as evidenced in Figure 7. An alternative explanation for the significant KIE observed in the formations of *tert*-butylbenzene and of *m*-*tert*-butyltoluene, the latter only at 120 °C, involves a rate-determining concerted process wherein the electrophilic attack proceeds simultaneously with the migration of H from the site of attack. This hypothesis, however, seems hardly compatible with the observed temperature dependence of  $k_{\text{H}}/k_{\text{D}}$ .

The above discussion lends support to the idea that the  $\text{Me}_3\text{C}^+$  attack at the para position of toluene is endowed with a higher degree of reversibility than the attack at the meta positions, i.e.,  $(k_2/k_{-1})_{\text{meta}} \gg (k_2/k_{-1})_{\text{para}}$ . The ultimate reason for this behavior lies in the fact that the isomeric 2- and 4-protonated 3-*tert*-butyltoluenes formed from the meta attack and the first ensuing H shift are the most stable species, toward which the system tends to evolve, consistent with previous results on the electrophilic *tert*-butylation of gaseous arenes.<sup>4</sup> As a matter of fact, the isomeric composition of the products reported in Tables I and II shows that formation of *m*-*tert*-butyltoluene increases at the expense of the para isomer with increasing temperature and decreasing base concentration, two factors which affect the internal energy and

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the lifetime of I. The questions arise as to which kind of reversibility is operative in the  $k_{-1}$  step or by which mechanism the *p-tert*-butyltoluenium  $\rightarrow$  *m-tert*-butyltoluenium isomerization takes place. At least three routes may be envisioned: (i) back dissociation of  $I_p$  to the collision complex or even to the free reactants, followed by further reaction to form  $I_m$  ( $I_m = I$ ,  $R = m\text{-Me}$ ); (ii) intramolecular 1,2 migration of a *tert*-butyl group, i.e.,  $I_p \rightarrow I_m$ ; (iii) intermolecular transfer of  $\text{Me}_3\text{C}^+$  from  $I_p$  to a second molecule of toluene forming  $I_m$ . Circumstantial, evidence favoring an isomerization via the collision complex (route i) rather than by 1,2-*tert*-butyl group migration (route ii) comes from the protonation-induced isomerization of *o-tert*-butyltoluene to both *m*- and *p-tert*-butyltoluenes.<sup>23</sup> The occurrence of route iii is suggested by a slight decrease in the extent of meta substitution when the toluene concentration is lowered (cf. the last two entries of Table II), suggestive of a transalkylation reaction involving an arene molecule. Similar transalkylation reactions of the type  $\text{Me}_3\text{CC}_6\text{H}_6^+ + \text{C}_6\text{H}_5\text{R} \rightarrow \text{Me}_3\text{CC}_6\text{H}_5\text{R}^+ + \text{C}_6\text{H}_6$  ( $R = \text{Me}$  or  $\text{Me}_3\text{C}$ ) have been suggested to occur in a CI ion source, based on the faster disappearance of  $\text{Me}_3\text{CC}_6\text{H}_6^+$  ion at increasing concentrations of  $\text{C}_6\text{H}_5\text{R}$ .

### Conclusions

The results provide a deeper insight into the detailed mechanism of gas-phase aromatic *tert*-butylation, especially as regards a sharp kinetic discrimination among its consecutive steps and the evaluation of their influence on the overall reaction rate. Under conditions ensuring compliance to thermal kinetics, gas-phase *tert*-butylation displays mechanistic features closely related to those of classical electrophilic substitution in condensed media, in particular, the present results provide conclusive evidence for the intermediacy and the mechanistic role of ipso-substituted arenium ions I in the gas phase as well as in solution. The basicity of the ipso-substituted carbon relative to the adjacent ring positions is the key factor which determines the lifetime and the fate of I, and hence the course and the net rate of the alkylation.

If the ipso-substituted ion I is stabilized by a suitably located activating group, e.g., in  $I_p$ , its lifetime, which depends on the sum of  $k_{-1}$  and  $k_2$ , is sufficiently long ( $10^{-8}$ – $10^{-7}$  s) to allow deprotonation by bases present in the gas at the concentrations typical of radiolytic experiments ( $10^{16}$ – $10^{17}$  molecule  $\text{cm}^{-3}$ ). On the other hand, the lifetime of unstabilized ions, as those from benzene and  $I_m$  ions from toluene, is appreciably shorter, reflecting the increase of  $k_{-1}$  and of  $k_2$ . The former increases, owing to the less favorable

energetics for the formation of the arenium ion I from the collision complex, which shifts to the left the equilibrium between the two adducts. The value of  $k_2$  is also expected to be larger in  $I_m$  than in  $I_p$  ions, since the proton shift from the ipso to an ortho position is thermodynamically favored in  $I_m$  and nearly thermoneutral in  $I_p$ . In the case of benzene the balance of  $k_{-1}$  and  $k_2$  makes proton shift from the ipso position kinetically significant over the entire temperature interval investigated, 47–120 °C, whereas in the case of toluene it becomes significant only at 120 °C.

Within this general reactivity pattern, this work has focused on the direct determination of the rate constant for 1,2-H(D) shift within arenium ions. The use of selectively deuterated toluenes has allowed the evaluation of the  $k_4$  and  $k_6$  rate constants, related to the H(D) shift, following  $\text{Me}_3\text{C}^+$  ion attack at the para position of *p*- $\text{MeC}_6\text{H}_4\text{D}$  and *m*- $\text{MeC}_6\text{H}_4\text{D}$ . The Arrhenius activation parameters obtained for the  $\text{II} \rightarrow \text{III D}$  shift,  $E_a = 7.6 \pm 0.2$  kcal  $\text{mol}^{-1}$  and  $\log A = 12.9 \pm 0.4$ , are a significant addition to the very limited set of data presently available on the rates of *thermal* H shifts within gaseous arenium ions.<sup>3g,7b</sup> Both the estimated  $k_6/k_4$  ratio and the analysis of the overall  $k_H/k_D$  values in the *tert*-butylation of  $\text{C}_6\text{H}_6$ – $\text{C}_6\text{D}_6$  mixtures concur with the conclusion that the primary kinetic isotope effect associated with 1,2-H shifts following the  $\sigma$ -complex formation are unexpectedly large for a H migration process involving a far from linear reaction coordinate.

The results concerning the reactions of  $\text{Me}_3\text{Si}^+$  with benzene and toluene fit into the general scheme which identifies the relative basicity of the ipso-substituted carbon as the paramount mechanistic factor. In fact, the silylated  $\sigma$  complexes VIII display hardly any tendency to undergo 1,2-H shifts, a behavior clearly related to the enhanced basicity of the ipso-trimethylsilylated position of VIII. The present findings confirm previous conclusions regarding the mechanism of gas-phase cationic silylation and of related alkyl- or proto-desilylation reactions.<sup>7b,9,16</sup>

The results bear witness to the powers of the radiolytic technique, underlining the advantages derived from its time resolution, of the order of the nanosecond, from its wide pressure range, extending to the high-pressure domain where thermal kinetics apply, and from the isolation of the end products, which allows full exploitation of isotopic labeling techniques. In this connection, it can be noted that the H/D isotope effect which represents one of the most significant and mechanistically informative features of the *thermal tert*-butylation reaction vanishes altogether when the reaction is studied by mass spectrometric techniques.

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