

Methylation of aromatics with Me_3S^+ , Me_3Se^+ , and Me_3Te^+ in superacid media *

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Abstract

Electrophilic reactivity of $\text{Me}_3\text{S}^+\text{OTf}$, $\text{Me}_3\text{Se}^+\text{OTf}$, and $\text{Me}_3\text{Te}^+\text{OTf}$ ($\text{OTf} = \text{trifluoromethanesulfonate}$) in superacid solvents towards aromatics has been demonstrated, indicative of protosolvation of the remaining lone pair on the onium ions. When dissolved in superacids, $\text{Me}_3\text{Se}^+\text{OTf}$ and $\text{Me}_3\text{Te}^+\text{OTf}$ show measurable changes in their NMR (^1H , ^{13}C , ^{77}Se , ^{125}Te) chemical shifts and one bond $^{77}\text{Se}-^{13}\text{C}$, $^{125}\text{Te}-^{13}\text{C}$ spin-spin coupling constants. The NMR data are compared with those of related selenonium cations and donor-acceptor complexes.

Introduction

Trialkyloxonium ion salts per se have no alkylating ability towards aromatics. However, in superacid solvents, as demonstrated by Olah and co-workers [1], $\text{Me}_3\text{O}^+\text{BF}_4^-$, $\text{Me}_3\text{O}^+\text{SbCl}_6^-$, and $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ alkylate aromatics such as benzene and toluene. This implies that a protolytic interaction occurs between the superacid proton and the remaining lone pair on the oxonium ion.

Olah [2], Mateescu [3] and collaborators have elegantly demonstrated the occurrence of H–D exchange in the parent ^{17}O -labeled isotopic hydronium ion ($\text{D}_2\text{H}^{17}\text{O}^+$, $\text{DH}_2^{17}\text{O}^+$) by ^{17}O NMR in the strongest superacid HF/SbF_5 (1/1) or DF/SbF_5 (1/1) with $H_0 = -25 \rightarrow -28$ [4], and the acidity dependency of the exchange [2], providing further evidence in support of protosolvation of oxonium ions in superacid media. High level theoretical calculations suggest that even though H_4O^{2+} is a minimum energy structure, its generation would require substantial solvent stabilization [2].

The possibility that other onium ions of group 16 (sulfonium, selenonium and telluronium ions) may be similarly proto-solvated in superacid media to give

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dications has not been addressed experimentally, nor are the energetics of the resulting onium dications available so as to provide a comparison of their stabilities with H_4O^{2+} .

On the assumption that the energetics of H_4Se^{2+} and H_4Te^{2+} are of the same order of magnitude (or higher) than those calculated for H_4O^{2+} , the equilibrium concentration of the protosolvated onium ions is expected to be quite small even in HF/SbF_5 (1/1).

In relation to our recent multinuclear NMR studies of selenonium and telluronium salts [5], we have now examined the alkylation behavior of $\text{Me}_3\text{S}^+ \text{OTf}^-$, $\text{Me}_3\text{Se}^+ \text{OTf}^-$ and $\text{Me}_3\text{Te}^+ \text{OTf}^-$ towards aromatics in superacid media. We have also measured the variations in chemical shifts and coupling constants of these onium ions upon protosolvation in superacids.

Results and discussion

When homogeneous solutions of $\text{Me}_3\text{S}^+ \text{OTf}^-$, $\text{Me}_3\text{Se}^+ \text{OTf}^-$, and $\text{Me}_3\text{Te}^+ \text{OTf}^-$ in dry CH_3CN solvent are allowed to react with excess toluene (8 fold) at room temperature for 12 h, GC analysis of the reaction mixtures shows no detectable xylene isomers. Hence a complete lack of methylating ability of the cation salts. Similar results are obtained in the absence of CH_3CN when slurries of the cation salts in excess toluene or anisole are vigorously mixed at room temperature for 12 h. Heating of the solutions was not attempted as the salts are thermally labile.

On the other hand, slow addition of a cold solution of the onium salts (Me_3S^+ , Me_3Se^+ , or Me_3Te^+) in $\text{FSO}_3\text{H} + \text{SbF}_5$ (1/1) SO_2 to excess (8 fold) cold toluene in Freon-113/ SO_2 initially at dry ice-acetone temperature to avoid overheating followed by slow warm-up to -20°C over a period of 15 minutes, shows xylene isomers (25%) after work up and capillary GC analysis. Unexpectedly, the major product of the reaction is *p*-tolyl sulfoxide (^{13}C and ^1H NMR, GC, GC-MS, and FD-MS) possibly formed through a fluorosulfonation/ionization/condensation sequence of toluene itself in magic acid. The "less unexpected" 4,4'-dimethylbiphenyl, a product of a Scholl type dehydrogenating condensation reaction under Friedel-Crafts conditions [6], was not observed. The methylation with the onium ions is, therefore, a competing (minor) pathway.

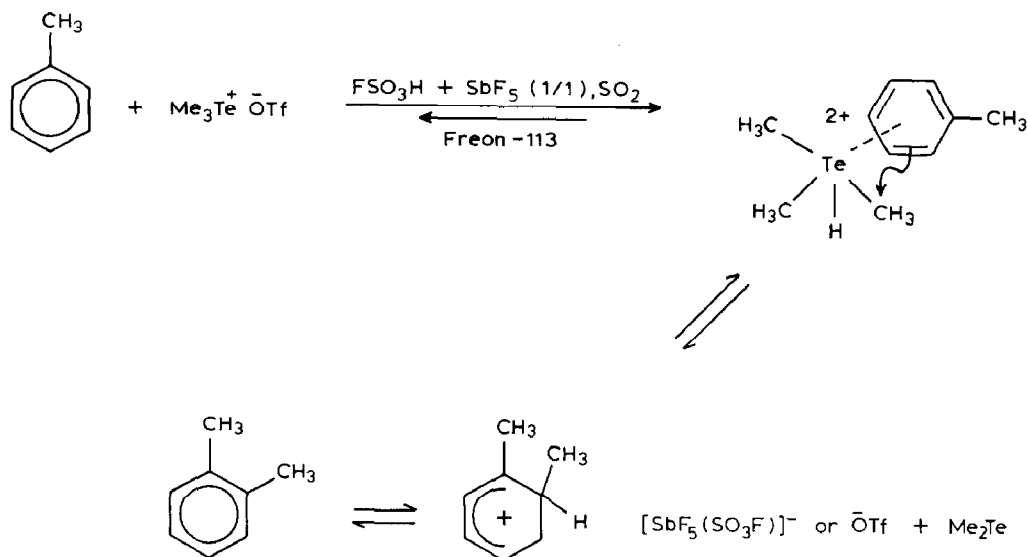
The acidity of the superacid (H_0) is crucial in the alkylation step with the studied onium ions, since xylenes are not detected in control experiments where magic acid ($H_0 = -21.5$) [7] is replaced by $\text{CF}_3\text{SO}_3\text{H}$ ($H_0 = -14.1$) [8]. The observed acidity

Table 1

Isomer distribution (%) in methylation of toluene with onium ion salts in magic acid solvent

Cation salt	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
$(\text{CH}_3)_3\text{O}^+ \text{BF}_4^-^a$	60	12	28
$(\text{CH}_3)_3\text{O}^+ \text{SbCl}_6^-^a$	68	11	21
$(\text{CH}_3)_3\text{S}^+ \text{OTf}^-$	78	4	18
$(\text{CH}_3)_3\text{Se}^+ \text{OTf}^-$	66	32	2
$(\text{CH}_3)_3\text{Te}^+ \text{OTf}^-$	93	6	1

^a Taken from ref. 1.



Scheme 1

dependency of alkylation is strongly indicative of a proto-solvated cation as the electrophile, and argues against the possibility that the role of acid is simply to solvate a tight ion pair.

In a control experiment the reaction of toluene itself in magic acid under the experimental condition used in our alkylations gave only *p*-tolyl sulfoxide (65% isolated yield) and no xylenes could be detected. Thus methyl disproportionation of toluene itself as a possible source of xylenes is excluded.

The isomer distributions are summarized in Table 1. The xylene isomer distribution formed via methylation with Me_3S^+ is close to that of Me_3O^+ , with the *ortho* isomer predominating, indicative of the similarity of the methylation mechanism in both cases. With Me_3Se^+ , however, the *meta* isomer increases at the expense of *para*. The isomer distribution with Me_3Te^+ is most remarkable in that it is approaching exclusive *ortho* methylation. Reproducible results were obtained irrespective of the method and rate of mixing in three independent runs.

A plausible mechanism (Scheme 1) which could explain the observed isomer distributions would be to consider a π -type interaction between the electron deficient protosolvated onium ion and the aromatic π -system, creating substantial steric hindrance for electrophilic substitution at the *para* position. The steric bulk of Me_3Te^+ is such that not only the *para* but also the *meta* positions are blocked. Alternatively, the much larger coordination sphere of protosolvated Me_3Te^+ as compared to Me_3Se^+ and Me_3S^+ may allow metal coordination with the C_1 , C_2 ring carbons, leading to preferential methylation at the *ortho* positions [9*].

Turning our attention to protosolvated selenonium and telluronium ions, we then examined superacid solutions of the ions directly by low temperature NMR.

When the onium salts ($\text{Me}_3\text{Se}^+ \text{OTf}^-$ and $\text{Me}_3\text{Te}^+ \text{OTf}^-$) are dissolved in $\text{FSO}_3\text{H} + \text{SbF}_5 (1/1)$, SO_2 solvent system at dry ice-acetone temperature (vortex) the resulting

* Reference numbers with an asterisk indicate notes in the list of references.

Table 2

Comparison of the NMR (^1H , ^{13}C , ^{77}Se , ^{125}Te) chemical shifts of $\text{Me}_3\text{S}^+ \text{OTf}$, $\text{Me}_3\text{Se}^+ \text{OTf}$ and $\text{Me}_3\text{Te}^+ \text{OTf}$ in SO_2 and in Superacid + SO_2

Onium Ion	Solvent system/Temperature	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	$\delta(^{77}\text{Se})$	$\delta(^{125}\text{Te})$
$\text{Me}_3\text{S}^+ \text{OTf}$	$\text{SO}_2 / -40^\circ \text{C}$	3.00	27.26		
$\text{Me}_3\text{S}^+ \text{OTf}$	$\text{FSO}_3\text{H} + \text{SbF}_5(1/1) / \text{SO}_2 - 70^\circ \text{C}$	3.27	27.05		
$\text{Me}_3\text{Se}^+ \text{OTf}$	$\text{SO}_2 / -40^\circ \text{C}$	2.76	21.78 ^a	255 ^a	
$\text{Me}_3\text{Se}^+ \text{OTf}$	$\text{FSO}_3\text{H} + \text{SbF}_5(1/1), \text{SO}_2 / -70^\circ \text{C}$	3.26	21.54	251	
$\text{Me}_3\text{Te}^+ \text{OTf}$	$\text{SO}_2 / -40^\circ \text{C}$	2.39	3.76		408
$\text{Me}_3\text{Te}^+ \text{OTf}$	$\text{FSO}_3\text{H} + \text{SbF}_5(1/1), \text{SO}_2 / -70^\circ \text{C}$	2.71	3.25		399
$\text{Me}_3\text{Te}^+ \text{OTf}$	$\text{HF} + \text{SbF}_5(1/1), \text{SO}_2 / -70^\circ \text{C}$	2.75	3.27		

^a Taken from ref. 5.

clear, almost colorless, solutions show the following changes in their NMR spectra:

- (a) the protons become deshielded,
- (b) the carbons become slightly shielded,
- (c) The ^{77}Se and ^{125}Te chemical shifts of the cationic centers are both shielded.

The relative magnitude of the shielding for ^{125}Te and ^{77}Se ($^{125}\text{Te}/^{77}\text{Se} = \text{ca. } 2.25$) closely parallels their relative sensitivity factor determined by McFarlane [10]. The methyl protons are even more deshielded in the much stronger superacid system $\text{HF} + \text{SbF}_5(1/1), \text{SO}_2$. Data are gathered in Table 2.

The ^{77}Se and ^{125}Te chemical shifts are influenced by both paramagnetic (δ^p) and diamagnetic (δ^d) shielding contributions. The diamagnetic contribution is small in most cases and rather insensitive to changes in bonding. Both selenium and tellurium chemical shifts are relatively insensitive to solvent effects [5,11*].

A consistent trend of increased shielding in onium ions [$\delta_{\text{H}} \text{R}_3\text{O}^+ > \text{R}_3\text{S}^+ > \text{R}_3\text{Se}^+ > \text{R}_3\text{Te}^+$], was established by Olah and co-workers reflecting charge delocalization and shielding by heavier atoms [12,13].

An increase in the electron-withdrawing ability of the ligands attached to selenium and tellurium is known to lead to an upfield shift, meaning that the P term in the Jameson–Gutowsky equation increases [10]. We find that this fits in with our observed shielding of ^{77}Se and ^{125}Te in magic acid.

We have also measured one-bond $^{77}\text{Se}-^{13}\text{C}$ and $^{125}\text{Te}-^{13}\text{C}$ coupling constants in the ^{13}C NMR spectra. The data are gathered in Table 3. It is known that in general the coupling constants involving ^{125}Te are almost twice as large compared to ^{77}Se coupling constants in analogous compounds [10].

In going from Me_2Se to Me_3Se^+ the $|J|$ decreases by 9.9 units (61 and 51.1, respectively). Similarly, the $^{125}\text{Te}-^{13}\text{C}$ coupling constant in going from Me_2Te to Me_3Te^+ decreases by 15.1 units (158.9 and 143.8, respectively). We have found a small but measurable decrease in the magnitude of the coupling constants of Me_3Se^+ and Me_3Te^+ dissolved in superacids.

A comparison of one bond coupling constants in model selenonium cations with those of the corresponding donor–acceptor complexes could provide additional insight. There is a consistent trend of coupling constants decrease with increased positive charge at the heavy nucleus, indicative of a decrease in the *s*-character in going from the donor–acceptor complex to the corresponding selenonium cation.

Table 3

Comparison of one bond $^{77}\text{Se}-^{13}\text{C}$ and $^{125}\text{Te}-^{13}\text{C}$ coupling constants of selenonium and telluronium ions in SO_2 with those in magic acid/ SO_2 and with related onium cations and donor-acceptor complexes

Onium ion	Solvent system temperature	$ ^1J $
Me_3Se^+	$\text{SO}_2 (-45^\circ\text{C})$	51.1 ^a
Me_3Se^+	$\text{FSO}_3\text{H} + \text{SbF}_5(1/1), \text{SO}_2 (-70^\circ\text{C})$	49.5
Me_3Se^+	$\text{HF} + \text{SbF}_5(1/1), \text{SO}_2 (-65^\circ\text{C})$	49.4
Me_3Te^+	$\text{SO}_2 (-40^\circ\text{C})$	143.8
Me_3Te^+	$\text{FSO}_3\text{H} + \text{SbF}_5(1/1), \text{SO}_2 (-70^\circ\text{C})$	143.3
$\text{Me}_2\text{Se}^+-\text{H}$	$\text{FSO}_3\text{H} + \text{SbF}_5(1/1), \text{SO}_2 (-70^\circ\text{C})$	57 ^a
$\text{Me}_2\text{Se}^{+\delta} \rightarrow \overset{\delta-}{\text{SbF}}_5$	$\text{SbF}_5/\text{SO}_2\text{ClF} (-60^\circ\text{C})$	68 ^a
$\text{Et}_2\text{Se}^+-\text{H}$	$\text{FSO}_3\text{H} + \text{SbF}_5(1/1), \text{SO}_2$	45 ^a
$\text{Et}_2\text{Se}^{+\delta} \rightarrow \overset{\delta-}{\text{SbF}}_5$	$\text{SbF}_5/\text{SO}_2\text{ClF} (-60^\circ\text{C})$	64 ^a

^a Taken from ref. 5.

In conclusion, it has been shown that protosolvated Me_3S^+ , Me_3Se^+ and Me_3Te^+ methylate aromatics in superacid media. Interaction with the aromatic system leads to unusual isomer distributions. When dissolved in superacid media at low temperature Me_3Se^+ and Me_3Te^+ show measurable changes in their NMR chemical shifts and one-bond $^{77}\text{Se}-^{13}\text{C}$, $^{125}\text{Te}-^{13}\text{C}$ coupling constants. The observed changes appear to be compatible with the notion that the onium ions are protosolvated and dications may be contributing species in a rapid equilibrium.

Experimental

The superacids used were freshly prepared from distilled FSO_3H and SbF_5 or HF and SbF_5 . $\text{CF}_3\text{SO}_3\text{H}$ (Aldrich) was doubly distilled prior to use. The aromatic substrates were highest purity commercial samples (Gold Label), the purity of which was checked by GC prior to use.

The onium ions were prepared by methylation of the corresponding dimethyl precursor with methyl triflate in Freon solvent. GC analyses were performed on a Hewlett-Packard 5890A instrument equipped with a 25 m OV101 and a 5m HP methyl silicone gum capillary columns.

NMR spectra were run on a Varian FT 80 instrument equipped with a broad band probe and a low temperature unit.

Alkylation of toluene with $\text{Me}_3\text{S}^+ \text{OTf}$, $\text{Me}_3\text{Se}^+ \text{OTf}$ and $\text{Me}_3\text{Te}^+ \text{OTf}$: In a typical experiment, to the onium salt (1 mmol) dissolved in SO_2 (1 ml) was added a clear solution of magic acid (1 ml) dissolved in SO_2 (1 ml) at dry ice-acetone temperature (Vortex) under a dry nitrogen atmosphere. The resulting homogeneous solution was added dropwise with a precooled pipet to a solution of excess toluene (8 mmol) diluted with a mixture of Freon-113 (10 ml) and SO_2 (2 ml) at dry ice-acetone temperature with vigorous mixing under nitrogen. The resulting slightly viscous blue colored solution was allowed to warm up slowly to -20°C over a period of 15 min, while vigorously mixing, after which the reaction mixture was carefully quenched in ice/bicarbonate, extracted with CH_2Cl_2 and analyzed by capillary GC. The xylene isomers were identified by coinjection with pure authentic samples. In general, reproducible results could be obtained within experimental

error irrespective of the rate of mixing and the method of addition of the onium cation salts in superacids to the aromatic compound. Thus the observed isomer distributions cannot be a consequence of mixing problems. The yield of xylenes was ca. 25% based on toluene reacted. The *p*-tolyl sulfoxide by-product was isolated by evaporation of the CH_2Cl_2 extracts or by addition of pentane and cooling.

Alternatively, it was crystallized from ethyl acetate by cooling (m.p. 94–96 °C). Its identity was confirmed by GC coinjection with an authentic sample on two different capillary columns (a 25m OV101 and a 5m HP methyl silicon gum), by comparison of ^{13}C and ^1H NMR data with an authentic sample, as well as by GC-MS and FD-MS ($M^+ = 230$). Whereas the ^1H NMR spectra of *p*-tolyl sulfoxide and 4,4'-dimethylbiphenyl are nearly identical, comparison of ^{13}C and mass spectral data, melting points, and GC coinjections clearly ruled out the latter.

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