Distinguishing Conventional and Distonic Radical Cations by Using Dimethyl Diselenide

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Dimethyl diselenide is demonstrated to be among the most powerful reagents used to identify distonic radical cations. Most such ions readily abstract $\text{CH}_3\text{Se}^\cdot$ from dimethyl diselenide. The reaction is faster and more exclusive than $\text{CH}_3\text{S}^\cdot$ abstraction from dimethyl disulfide, a reaction used successfully in the past to identify numerous distonic ions. Very acidic distonic ions, such as $\text{HC}^+(\text{OH})\text{OCH}_2$, do not undergo $\text{CH}_3\text{Se}^\cdot$ abstraction, but instead protonate dimethyl diselenide. In sharp contrast to the reactivity of distonic ions, most conventional radical cations were found either to react by exclusive electron transfer or to be unreactive toward dimethyl diselenide. Hence, this reagent allows distinction of distonic and conventional isomers, which was demonstrated directly by examining two such isomer pairs. To be able to predict whether electron transfer is exothermic (and hence likely to occur), the ionization energy of dimethyl diselenide was determined by bracketing experiments. The low value obtained (7.9 ± 0.1 eV) indicates that dimethyl diselenide will react with many conventional carbon-, sulfur-, and oxygen-containing radical cations by electron transfer. Nitrogen-containing conventional radical cations were found either to react with dimethyl diselenide by electron transfer or to be unreactive. © 1996 American Society for Mass Spectrometry (*J Am Soc Mass Spectrom* 1996, 7, 1245–1250)

Knowledge concerning the structures of organic radical cations is crucial for numerous applications of mass spectrometry, ranging from attempts to advance the fundamental understanding of ionic gas-phase processes to interpretation of unknown mass spectra. Many conventional organic radical cations (e.g., molecular ions) have been demonstrated to isomerize to a *distonic ion* (formally an ionized biradical, zwitterion, or ylide) [1]. Hence, a simple method that would allow the unambiguous identification of distonic ions would be invaluable.

Dimethyl disulfide is among the reagents commonly used [2] to identify distonic ions. Most such ions react with CH_3SSCH_3 by $\text{CH}_3\text{S}^\cdot$ abstraction while conventional radical cations either react by electron transfer or are unreactive. This approach is not universally applicable, however. Some distonic ions react with CH_3SSCH_3 by electron transfer in addition to $\text{CH}_3\text{S}^\cdot$ abstraction. For example, $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^\cdot$ reacts with CH_3SSCH_3 by these two pathways in about a 1:1 ratio [2]. The observation of electron transfer complicates the interpretation of the data because it is unknown whether the species undergoing this reaction is a distonic ion or whether part of the ion population

has a conventional structure. Further complications arise from the facts that many distonic ions are unreactive toward CH_3SSCH_3 , and that those ions that do undergo $\text{CH}_3\text{S}^\cdot$ abstraction react only slowly (usually less than one of five collisions leads to $\text{CH}_3\text{S}^\cdot$ abstraction) [2–4].

As an attempt to address the foregoing problems, dimethyl diselenide was recently examined [5] as an alternative reagent for identifying distonic ions. We provide here a comprehensive evaluation of the effectiveness of $\text{CH}_3\text{SeSeCH}_3$ as a tool for distinguishing distonic and conventional radical cations, and examine the advantages of the use of this reagent over the use of CH_3SSCH_3 . Finally, the ionization energy of dimethyl diselenide was determined. This value allows one to predict when electron transfer reactions are to be expected.

Experimental

All compounds used were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used as received, with the exception of dimethyl diselenide (a toxic chemical), which was purified by vacuum distillation at 0.1 torr (b.p. 156°C). The purity of all reagents was checked by gas chromatography and by mass spectrometry.

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The experiments were carried out in an Extrel FTMS/2001 Fourier transform ion cyclotron resonance mass spectrometer (Finnigan FTMS, Madison, WI). This instrument contains a dual cell that consists of two identical cubic 2-in. cells joined by a common wall (the conductance limit). The cell is aligned collinearly within the magnetic field produced by a 3.0-T superconducting magnet operated at approximately 2.5 T. The conductance limit and the two end trapping plates were held at +2.0 V to trap positive ions within the cell. The cell was differentially pumped with two Balzer (Arlington Heights, IL) turbomolecular pumps (330 L/s), each of which was backed with an Alcatel (Hingham, MA) 2012 mechanical pump. A nominal base pressure of $< 1 \times 10^{-9}$ torr was maintained within the cell, as read with two ion gauges.

Samples were introduced into the instrument by using two Extrel single batch inlet systems equipped with a variable leak valve (nominal pressures $\approx 1.0 \times 10^{-7}$ torr). Before introduction into the cell, dimethyl diselenide was degassed several times by freezing the sample with liquid nitrogen, pumping away the air, and allowing the sample to warm up to room temperature. The reactant ions were generated in one side of the dual cell by electron ionization or by ion–molecule reactions. The ion signal was optimized by varying the electron beam time (30–70 ms), emission current (3–8 μ A), electron energy (20–70 eV), and reaction time. All ions were removed from the other cell region by changing its end trapping plate voltage from +2.0 to –2.0 V for 10–15 ms. The ions were transferred into this cell region by grounding the conductance limit plate for approximately 100 μ s. The ions were cooled by collisions with argon introduced into the instrument through a pulsed-valve system. All unwanted ions were ejected by applying stored waveform inverse Fourier transform (SWIFT) [6] excitation pulses to the excitation plates by using an Extrel SWIFT module. The isolated ion was then allowed to react with neutral reagents for a variable period of time. Each reaction spectrum was background corrected by using a previously described procedure [7].

The product ions were excited for detection by applying an excitation sweep of 124- V_{p-p} amplitude, 2.7-MHz bandwidth, and 3.2-kHz/ μ s sweep rate or by the SWIFT method (17–800 u, 0.5-cm radius for all ions). A minimum of 20 acquisitions were signal averaged to improve the signal-to-noise ratio. The spectra were recorded as 32k data points, by using one zero fill prior to Fourier transformation.

The pressure gradient between the ion gauges and the cell must be accounted for when estimating the actual pressure in the cell [8a]. The sensitivity of the ion gauges toward different neutral reagents also varies [8b]. To compensate for these differences, an ion gauge correction factor was obtained by measuring the rates of several proton and/or electron transfer reactions with known rate constants involving each neutral reagent. The ion gauge correction factor used in the

calculation of rate constants for the reactions involving neutral dimethyl diselenide is 1.8.

Reaction rate constants (k_{exp}) were determined from plots of $\ln(\text{relative reactant ion abundance})$ as a function of reaction time. Collision rate constants (k_{coll}) were calculated by using a literature procedure [9]. The polarizability of dimethyl diselenide (necessary for the calculation of k_{coll}) was estimated to be $12.32 \text{ \AA}^3$ [10]. The reaction efficiency is given by $k_{\text{exp}}/k_{\text{coll}}$. Primary products were identified based on their fixed relative abundances at short reaction times.

Results and Discussion

Reactivity

In relation to the sulfur–sulfur bond in CH_3SSCH_3 , the relatively large outer orbitals of selenium cause the Se–Se homolytic bond dissociation energy to be lower [11], thereby allowing this bond to be readily cleaved. Indeed, the distonic ions studied show a more efficient abstraction of a $\text{CH}_3\text{Se}^\cdot$ group from $\text{CH}_3\text{SeSeCH}_3$ (Table 1) than $\text{CH}_3\text{S}^\cdot$ from CH_3SSCH_3 . For example, $^\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ (ionized cyclobutanone), an ion that has been well-characterized by theoretical and experimental methods [2, 12], reacts with $\text{CH}_3\text{SeSeCH}_3$ by a rapid and exclusive $\text{CH}_3\text{Se}^\cdot$ abstraction (Table 1). This distonic ion reacts only slowly with CH_3SSCH_3 , yielding the electron transfer product ($\text{CH}_3\text{SSCH}_3^+$) as well as the structurally characteristic $\text{CH}_3\text{S}^\cdot$ abstraction product. Furthermore, the aromatic distonic ions *N*-(3-dehydrophenyl)-3-fluoropyridinium ion (Figure 1a) and 4-dehydrophenyldimethyl sulfonium ion react with $\text{CH}_3\text{SeSeCH}_3$ by $\text{CH}_3\text{Se}^\cdot$ abstraction approximately three times faster than they react with CH_3SSCH_3 (the reaction efficiencies are 25 and 14% versus 7 and 5%, respectively; Table 1). Similarly, the prototypical organophosphorus distonic ion $^\cdot\text{CH}_2\text{PH}_3^+$ reacts with $\text{CH}_3\text{SeSeCH}_3$ by exclusive $\text{CH}_3\text{Se}^\cdot$ abstraction at 75% of the collision rate (Figure 1c; Table 1), whereas the reaction with CH_3SSCH_3 yields both the electron transfer and $\text{CH}_3\text{S}^\cdot$ abstraction products (at 40% of the collision rate) [13].

The facile $\text{CH}_3\text{Se}^\cdot$ abstraction observed for distonic ions can be used to distinguish them from their conventional isomers. For example, while the ion $^\cdot\text{CH}_2\text{PH}_3^+$ reacts with $\text{CH}_3\text{SeSeCH}_3$ by $\text{CH}_3\text{Se}^\cdot$ abstraction, its conventional isomer CH_3PH_2^+ yields only the electron transfer product (Table 2) [13]. Similarly, electron transfer is the only reaction observed for the conventional radical cation of trimethylene oxide, while its ring-opened distonic form $^\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ yields several products, including that formed by $\text{CH}_3\text{Se}^\cdot$ abstraction (Tables 1 and 2). Some of the product ions formed upon $\text{CH}_3\text{Se}^\cdot$ abstraction from this distonic ion are unstable and spontaneously lose CH_2O . The same applies to the lower homolog $^\cdot\text{CH}_2\text{OCH}_2^+$ (Table 1). Similarly, loss of CH_2O has been reported for the

Table 1. Reactions of distonic ions with dimethyl diselenide

Distonic ion	Product ion ^a	Observed reaction	Reaction efficiency(%)
m/z 70	m/z 165	$\text{CH}_3\text{Se}^\cdot$ abstraction (100%)	64
m/z 44	m/z 109	$\text{CH}_3\text{Se}^\cdot$ abstraction-OCH ₂ (100%)	100
m/z 68	m/z 163	$\text{CH}_3\text{Se}^\cdot$ abstraction (100%)	66
m/z 60	m/z 191	proton transfer (100%)	b
m/z 58	m/z 123 m/z 153 $(m/z$ 190	$\text{CH}_3\text{Se}^\cdot$ abstraction-OCH ₂ (45%) $\text{CH}_3\text{Se}^\cdot$ abstraction (55%) electron transfer) ^c	b
m/z 48	m/z 143	$\text{CH}_3\text{Se}^\cdot$ abstraction (100%)	68
m/z 173	m/z 268	$\text{CH}_3\text{Se}^\cdot$ abstraction (100%)	25
m/z 138	m/z 233	$\text{CH}_3\text{Se}^\cdot$ abstraction (100%)	14

^a The ion containing the major isotope of Se is indicated.^b Fast reaction.^c Trace.

$\text{CH}_3\text{S}^\cdot$ abstraction products formed from these two ions upon reaction with CH_3SSCH_3 [2].

The only distonic ion that does not show $\text{CH}_3\text{Se}^\cdot$ abstraction is the acidic distonic ion $\text{HC}^+(\text{OH})\text{OCH}_2^\cdot$. This ion reacts with $\text{CH}_3\text{SeSeCH}_3$ by proton transfer (Table 1; the same reaction has been reported [2] for CH_3SSCH_3). The reactivity demonstrated by $\text{HC}^+(\text{OH})\text{OCH}_2^\cdot$, although not similar to that described above for other distonic ions, nevertheless distinguishes this ion from conventional radical cations whose reactivity is quite different, as discussed above and in subsequent text.

In sharp contrast to the behavior observed for distonic radical cations, most conventional radical cations react with $\text{CH}_3\text{SeSeCH}_3$ by electron transfer (Table 2). Two ions hold exception to this observation. The conventional radical cations $(\text{CH}_3)_3\text{P}^{+\cdot}$ and $(\text{CH}_3\text{O})_3\text{P}^{+\cdot}$ have been reported to react with $\text{CH}_3\text{SeSeCH}_3$ by $\text{CH}_3\text{Se}^\cdot$ abstraction (Table 2) [14]. Analogously, $\text{CH}_3\text{S}^\cdot$

abstraction occurs upon reaction of these ions with CH_3SSCH_3 [14]. A two-step mechanism has been used to rationalize [14] this reactivity. Electron transfer between the radical cations and $\text{CH}_3\text{SeSeCH}_3$ (or CH_3SSCH_3) is thought to lead to a long-lived ion-molecule complex wherein $\text{CH}_3\text{SeSeCH}_3^{+\cdot}$ (or $\text{CH}_3\text{SSCH}_3^{+\cdot}$) suffers a nucleophilic attack by the neutral phosphorus compound to generate the observed ionic product [14]. In support of this mechanism, $(\text{CH}_3)_3\text{P}$ and $(\text{CH}_3\text{O})_3\text{P}$ were shown to replace $\text{CH}_3\text{S}^\cdot$ in $\text{CH}_3\text{SSCH}_3^{+\cdot}$. The fact that the recombination energies of $(\text{CH}_3)_3\text{P}^{+\cdot}$ and $(\text{CH}_3\text{O})_3\text{P}^{+\cdot}$ are close to the ionization energies of $\text{CH}_3\text{SeSeCH}_3$ and CH_3SSCH_3 , together with the nucleophilic character of the neutral phosphorus compounds, makes the observed reactivity possible (the ionization energies of $(\text{CH}_3)_3\text{P}$ and $(\text{CH}_3\text{O})_3\text{P}$ are 8.06 and 8.5 eV, respectively [15]). This reactivity is not expected for most organic radical cations [14].

Figure 1. (a) Reaction of the *N*-(3-dehydrophenyl)-3-fluoropyridinium ion (m/z 173) for 6.5 s with dimethyl diselenide (nominal pressure 9.5×10^{-8} torr). $\text{CH}_3\text{Se}^\cdot$ abstraction was observed. (b) Reaction of $\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}^+\text{O}$ (m/z 68) for 1.2 s with dimethyl diselenide (nominal pressure 1.2×10^{-7} torr). $\text{CH}_3\text{Se}^\cdot$ abstraction observed. (c) Reaction of CH_2PH_3^+ (m/z 48) for 1.6 s with dimethyl diselenide (nominal pressure 4.6×10^{-8} torr). $\text{CH}_3\text{Se}^\cdot$ abstraction was observed.

The occurrence of $\text{CH}_3\text{Se}^\cdot$ abstraction for distonic ions but not for analogous even-electron ions provides strong support for bond formation at the radical site upon $\text{CH}_3\text{Se}^\cdot$ abstraction. For example, the even-electron ions *N*-phenyl-3-fluoropyridinium and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$ are unreactive toward $\text{CH}_3\text{SeSeCH}_3$, while the related distonic ions, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ and *N*-(3-dehydrophenyl)-3-fluoropyridinium ion, undergo $\text{CH}_3\text{Se}^\cdot$ abstraction (Table 1, Figure 1a).

Ionization Energy

Data concerning the adiabatic ionization energy of $\text{CH}_3\text{SeSeCH}_3$ is necessary to be able to predict which radical cations will react with this reagent by electron

transfer. An approximate ionization energy of 8.1 eV has been determined for $\text{CH}_3\text{SeSeCH}_3$ by photoelectron spectroscopy [15, 16]. Bracketing experiments were employed to obtain another estimate for the adiabatic ionization energy of $\text{CH}_3\text{SeSeCH}_3$.

Neutral $\text{CH}_3\text{SeSeCH}_3$ was reacted with conventional reference radical cations of known structures and recombination energies (ionization energies of the corresponding neutral molecules) ranging between 7.1 and 9.7 eV [15, 17]. Since endothermic processes cannot occur under the conditions employed here, the occurrence of electron transfer implies that the reaction is thermoneutral or exothermic. The observation of electron transfer from $\text{CH}_3\text{SeSeCH}_3$ to ionized 1-methylpyrrole indicates that the ionization energy of $\text{CH}_3\text{SeSeCH}_3$ is less than 7.94 eV (Table 3). On the other hand, the ionization energy of $\text{CH}_3\text{SeSeCH}_3$ is concluded to be greater than 7.82 eV based on the absence of electron transfer between $\text{CH}_3\text{SeSeCH}_3$ and ionized trimethylamine (Table 3). The bracketing of the ionization energy of $\text{CH}_3\text{SeSeCH}_3$ between 7.82 and 7.94 eV was probed by examination of reactions of several other reference ions. All the conventional radical cations that were observed to undergo electron transfer with $\text{CH}_3\text{SeSeCH}_3$ have a recombination energy greater than 7.94 eV, and those that do not react by electron transfer have a recombination energy less than 7.82 eV (Table 3).

The accuracy of the preceding findings was confirmed by examination of the reverse reactions (Table 3). In these experiments, $\text{CH}_3\text{SeSeCH}_3$ was ionized and reacted with the neutral precursors of the reference radical cations. In agreement with the above results, $\text{CH}_3\text{SeSeCH}_3^+$ reacts by electron transfer with trimethylamine, but not with 1-methylpyrrole. All the neutral compounds that were found to undergo electron transfer with $\text{CH}_3\text{SeSeCH}_3^+$ have an ionization energy less than 7.82 eV, and those that do not show electron transfer have an ionization energy greater than 7.94 eV (Table 3). Hence, the adiabatic ionization energy of $\text{CH}_3\text{SeSeCH}_3$ is concluded to be 7.9 ± 0.1 eV and $\Delta H_f(\text{CH}_3\text{SeSeCH}_3^+) = 193$ kcal/mol (the latter value is 4 kcal/mol lower than the previously reported value) [15].

Conclusions

Nonacidic distonic ions were demonstrated to abstract $\text{CH}_3\text{Se}^\cdot$ from $\text{CH}_3\text{SeSeCH}_3$ more rapidly and more exclusively than they abstract $\text{CH}_3\text{S}^\cdot$ from CH_3SSCH_3 , a reagent commonly employed to identify distonic ions in the gas phase. Hence, $\text{CH}_3\text{SeSeCH}_3$ provides a more generally useful tool for the identification of distonic ions. The adiabatic ionization energy of $\text{CH}_3\text{SeSeCH}_3$ was bracketed to be 7.9 ± 0.1 eV. Since the typical range of ionization energies encountered for carbon-, oxygen- and sulfur-containing organic compounds is 8–10 eV, electron transfer is expected to

Table 2. Reactions of conventional radical cations with dimethyl diselenide

Conventional ion	Product ion ^a	Observed reaction
$\text{P}(\text{OCH}_3)_3^{+\cdot}$ m/z 124	m/z 219	$\text{CH}_3\text{Se}^\cdot$ abstraction (100%)
$\text{P}(\text{CH}_3)_3^{+\cdot}$ m/z 76	m/z 171	$\text{CH}_3\text{Se}^\cdot$ abstraction (100%)
$\text{CH}_3\text{PH}_2^{+\cdot}$ m/z 48	m/z 190	Electron transfer (100%)
$\text{CH}_3\text{SCH}_3^{+\cdot}$ m/z 62	m/z 190	Electron transfer (100%)
$\text{C}_6\text{H}_5\text{OCH}_3^{+\cdot}$ m/z 108	m/z 190	Electron transfer (100%)
$\text{C}_4\text{H}_7\text{O}^{+\cdot}$ m/z 84	m/z 190	Electron transfer (100%)
$\text{C}_3\text{H}_5\text{O}^{+\cdot}$ m/z 58	m/z 190	Electron transfer (100%)
$\text{C}_4\text{H}_8\text{N}^{+\cdot}\text{CH}_3$ m/z 81	m/z 190	Electron transfer (100%)
$\text{C}_6\text{H}_5\text{SCH}_3^{+\cdot}$ m/z 124	m/z 190	Electron transfer (100%)
$\text{C}_6\text{H}_{11}\text{N}^{+\cdot}\text{H}$ m/z 85	m/z 190	Electron transfer (100%)
$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2^{+\cdot}$ m/z 121	None	No reaction
$\text{C}_6\text{H}_5\text{NH}_2^{+\cdot}$ m/z 93	None	No reaction
$\text{N}(\text{CH}_3)_3^{+\cdot}$ m/z 59	None	No reaction

^a The ion containing the major isotope of Se is indicated.

Table 3. Bracketing of the ionization energy of dimethyl diselenide

Neutral molecule	Adiabatic ionization energy ^a (eV)	M ⁺ + CH ₃ SeSeCH ₃	CH ₃ SeSeCH ₃ ⁺ + M
Trimethylene oxide	9.668 ± 0.005	+ ^b	- ^c
Cyclopentanone	9.25 ± 0.01	+	-
Methyl phosphine	9.12 ± 0.07	+	^d
Dimethyl sulfide	8.69 ± 0.01	+	^d
Anisole	8.21 ± 0.02	+	-
Piperidine	8.05 ± 0.05	+	-
Thioanisole	7.94 ± 0.02	+	-
1-Methylpyrrole	7.94 ± 0.02	+	-
Trimethylamine	7.82 ± 0.06	-	+
Aniline	7.67 ± 0.03 ^e	-	+
N,N-Dimethylaniline	7.12 ± 0.02	-	+

^a Reference 15 unless otherwise noted.^b The plus (+) indicates that an electron transfer reaction was the only reaction observed.^c The minus (-) indicates that no reaction was observed.^d Reaction not examined.^e Reference 17.

dominate the reaction of the conventional radical cations of these compounds with CH₃SeSeCH₃. Indeed, most of the conventional radical cations examined were found to react with CH₃SeSeCH₃ by electron transfer.

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