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Reactivity of the Gaseous Radical Cations of Trimethylenemethane and 2-Isopropylidenecyclopentane-1,3-diyl

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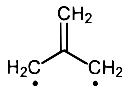
The radical cation of trimethylenemethane (TMM$^{\bullet+}$) and a derivative, 2-isopropylidenecyclopentane-1,3-diyl, were generated by electron ionization of methylenecyclopropane (MCP) and electron-ionization-induced loss of nitrogen from 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene, respectively, in a Fourier transform ion cyclotron resonance mass spectrometer. The two radical cations were isolated and their products and reaction rates with various gaseous reagents were measured. TMM$^{\bullet+}$ displays radical-type reactivity, e.g., it slowly abstracts a hydrogen atom from benzeneselenol and a thio- or selenomethyl radical from dimethyl disulfide and dimethyl diselenide, respectively. This reactivity distinguishes it from the isomeric 1,2- and 1,3-butadiene radical cations. Surprisingly, however, the TMM$^{\bullet+}$ undergoes electron transfer reactions in addition to radical reactions. The difference between the adiabatic recombination energy of TMM$^{\bullet+}$ (9.2 ± 0.1 eV) and the adiabatic ionization energy of MCP (9.4 ± 0.1 eV; the earlier literature estimate is ≤9.57 eV), which were experimentally determined in this work, indicates that the above electron abstraction reactions likely involve cyclization to yield MCP (and not TMM) as the final neutral product. In sharp contrast to TMM$^{\bullet+}$, the sterically hindered 2-isopropylidenecyclopentane-1,3-diyl radical cation is unreactive toward most of the reagents studied, including benzeneselenol, dimethyl disulfide, and dimethyl diselenide. The recombination energy of this TMM-type radical cation (and thus, the ionization energy of the 2-isopropylidenecyclopentane-1,3-diyl biradical) was measured to be 7.8 ± 0.1 eV.

Introduction

Trimethylenemethane (TMM, **1**) is an important member of a class of compounds known as non-Kekulé molecules.[1] Interest in TMM covers a wide range of areas, including organic synthesis,[2] study of reaction mechanisms,[1,3] computational chemistry,[4] and biological reactions.[5] The ionized derivatives of TMM (**2**, **3**) are a special class of distonic ions[6] (ionized biradicals, zwitterions, and ylides) wherein both the charge and the unpaired electron may be delocalized but over a different set of atoms. These intriguing charge and spin distributions have inspired the study of the properties of several negatively charged TMM derivatives in the gas phase, including the reduced form of TMM (**3**) and the related tetramethyleneethane (**4**).[7,8] In sharp contrast, positively charged TMM derivatives have received little attention. Most notably, no publications have appeared on the oxidized form of TMM (TMM$^{\bullet+}$). The reactivities of two of its higher homologues, **7** and **9**, have been studied in the condensed phase[9,10] (**7** also in the gas phase[9c]).



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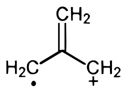

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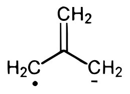

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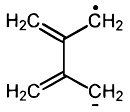

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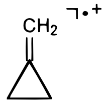

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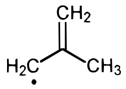

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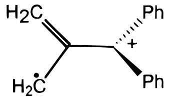

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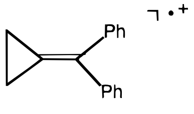

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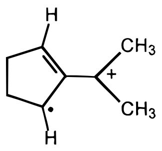

9

Theoretical work carried out by Du and Borden indicates that the ground electronic state of MCP$^{\bullet+}$ ($^2B_1$) lies 6.5 and 3.8 kcal mol^{-1} higher in energy than the $^2B_1$ and $^2A_2$ states of TMM$^{\bullet+}$, respectively (CISD/6-31G*(SVP)//CISD/6-31G*(SVP) level of theory).[11] Isomerization of the methylenecyclopropane radical cation (MCP$^{\bullet+}$, **5**) to TMM$^{\bullet+}$ was calculated to occur with little (about 2 kcal mol^{-1}) or no barrier. Hence, electron ionization of MCP is expected to provide a convenient route to TMM$^{\bullet+}$ in the gas phase. This approach was used here to generate

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$TMM^{\bullet+}$ for the examination of its reactivity in a Fourier transform ion cyclotron resonance mass spectrometer. The results are compared to those obtained for a related radical cation **9**, generated from 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene by electron-ionization-induced loss of nitrogen.

Experimental Section

Most of the reagents used were commercially available and used as received. The purity of the reagents was checked by mass spectrometry and gas chromatography. Methylenecyclopropane and 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene were synthesized according to literature procedures.[12]

Experiments were conducted utilizing an Extrel FTMS model 2001 Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer that has been described elsewhere.[13] The instrument consists of two adjacent 4.7 cm cubic cells housed within a 3 T superconducting magnet operated at about 2.7 T. Differential pumping of the cells was accomplished with two Balzers turbomolecular pumps (330 L s^{-1}), each of which is backed with an Alcatel 2012 mechanical pump. Typical nominal base pressure is less than 1×10^{-9} Torr in each cell. The pressure was monitored through the use of two MKS 290 ion gauges, one located near each cell. A literature procedure was used to correct the pressure readings for the varying sensitivity of ion gauges toward different neutral reagents.[14] The ion gauges were also calibrated for each neutral reagent by determining the rates of exothermic proton and electron transfer reactions.

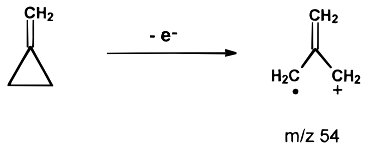
A typical experiment consisted of five steps: ion formation, transfer of the ions into a clean cell, cooling, isolation, and reactions. Neutral reagents were introduced into each cell at a nominal pressure of $(6-12) \times 10^{-8}$ Torr through an Extrel manufactured single batch inlet system equipped with a variable leak valve, or by using a Varian leak valve. The ion of interest was generated by electron ionization of the appropriate neutral precursor. Ionization conditions (40−70 eV electron energy, 20−70 ms ionization time, 5−8 μA emission current) were varied in order to maximize the signal of the desired ions. The ions were trapped in either cell by applying a 2.0 V potential to the trapping plates.

Ions that were formed in the first cell were transferred into the second cell by temporarily grounding the conductance limit (the middle trapping plate) for 50−90 μs so that the ions could pass through a 2 mm hole in this plate. *Prior to* ion transfer, all unwanted ions in the second cell were ejected by applying a −3.5 V potential to the remote trapping plate of the second cell. The ions were collisionally cooled by pulsing argon into the second cell (the nominal peak pressure was up to 1×10^{-5} Torr in the cell). Under these conditions, the ions undergo multiple collisions with argon atoms which results in vibrational and translational cooling.

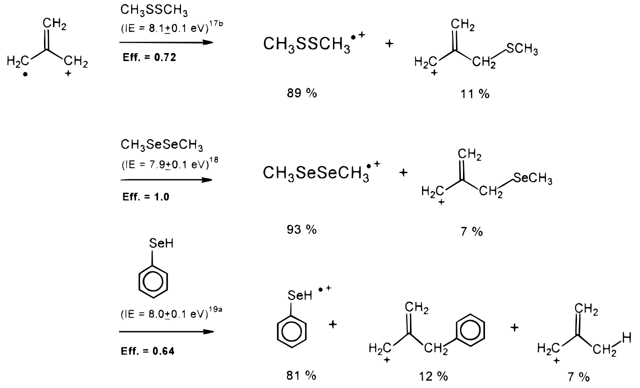
The ion of interest was isolated by using the stored waveform inverse Fourier transform (SWIFT) method to generate rf pulses that eject all undesired ions from the second cell. Subsequently, the isolated ion was allowed to undergo reactions with a neutral reagent present at a static pressure (nominal pressure 6×10^{-8} Torr). The reactions were monitored for a variable time period until at least 90% of the reactant ions were consumed.

Detection of ions was achieved by using a SWIFT waveform to excite all ions with *m*/*z* values of 10−800 to cyclotron radii of 0.5 cm. The spectra were recorded as 64*k* data points and collected with one zero fill prior to Fourier transformation. A background reaction spectrum was collected in the same manner but by ejecting the reactant ion from the cell *prior to* the reaction period.This spectrum was subtracted from the actual reaction spectrum in order to correct for reaction products arising from impurity ions not ejected from the cell during the ion isolation process.

SCHEME 1



SCHEME 2



Experimental second-order reaction rate constants (k_{exp}) were determined from the decay of the reactant ion signal as a function of reaction time. The rate constants obtained have an estimated accuracy of ±50% with a precision of better than ±10%. A parametrized trajectory theory was used to calculate the collision rate constants (k_{coll}).[15] Reaction efficiencies are given as k_{exp}/k_{coll}.

Results and Discussion

TMM Radical Cation. Dimethyl disulfide, dimethyl diselenide, and benzeneselenol were chosen to probe the reactivity of $TMM^{\bullet+}$ since the reactions of a variety of organic radical cations have been studied with these substances. Dimethyl disulfide and dimethyl diselenide are well-established probes for the identification of distonic radical cations.[17,18] These compounds usually react with radical cations by one of two reaction channels: electron transfer if the ion has a conventional structure, or transfer of $CH_3S^{\bullet}$ or $CH_3Se^{\bullet}$ if it has a distonic tructure. Benzeneselenol is an efficient hydrogen atom donor that readily transfers a hydrogen atom to most radicals and distonic radical cations (also to some conventional radical cations).[19]

$TMM^{\bullet+}$ was formed by electron ionization of methylenecyclopropane (MCP; Scheme 1), isolated, and allowed to interact with the selected neutral reagents for variable periods of time. The three reagents react with $TMM^{\bullet+}$ via the expected radical pathways (Scheme 2). Specifically, benzeneselenol, dimethyl disulfide, and dimethyl diselenide transfer a hydrogen atom, $CH_3S^{\bullet}$, or $CH_3Se^{\bullet}$ to $TMM^{\bullet+}$, respectively. Surprisingly, a fast electron transfer competes with all these reactions. At first glance, this finding seems to suggest that the reactant ion population consists of a mixture of $MCP^{\bullet+}$ (**5**) and $TMM^{\bullet+}$. This sort of discovery would not be unprecedented as electron ionization of 2,2-diphenyl-1-methylenecyclopropane and 1-(diphenylmethylene)cyclopropane produces a mixture of the cyclic ion (**8**) and the $TMM^{\bullet+}$ derivative (**7**).[9c] However, all the reactions studied were found to follow pseudo-first-order kinetics and proceed to completion. This result demonstrates that isomers with greatly differing chemical properties (as

TABLE 1: Reactions between the Trimethylenemethane Radical Cation and Selected Neutral Reagents of Known Ionization Energy

neutral reagent	ionization energy (eV)[a]	result
iodomethane	9.54 ± 0.05	−[b]
methanethiol	9.4386 ± 0.05	−
tetrahydrofuran	9.38 ± 0.05	−
ethyl iodide	9.35 ± 0.01	−
3-pentanone	9.31 ± 0.01	−
allyl iodide	9.298	−
cyclopentanone	9.25 ± 0.02	−
1,4-dioxane	9.19 ± 0.01	+[c]
2-iodobutane	9.10 ± 0.02	+
bromobenzene	9.00 ± 0.02	+
furan	8.88 ± 0.01	+
tert-butyl peroxide	8.4	+

[a] Reference 16. [b] Fast reactions other than electron transfer were observed. [c] Electron transfer was observed as the major reaction channel.

expected for $MCP^{\bullet+}$ and $TMM^{\bullet+}$) cannot be present in the reactant ion population, and strongly suggests that the ion population is isomerically pure.

The possibility of a complete isomerization of the $TMM^{\bullet+}$ population to yield an isomerically pure straight-chain isomer, either 1,2- or 1,3-butadiene radical cation, is ruled out based on the examination of the reactions of the authentic 1,2- and 1,3-butadiene radical cations. These radical cations react with dimethyl disulfide and benzeneselenol by exclusive, facile electron transfer. Hence, the ion population cannot be composed solely of these ions. Further support for this conclusion comes from the recombination energy measurements discussed below; the recombination energy determined for the $TMM^{\bullet+}$ ion population (9.2 eV) is distinctly different from the ionization energies reported for the two butadienes in the literature[16b] (9.0 eV).

The reactant ion population is concluded to consist of either $MCP^{\bullet+}$ or $TMM^{\bullet+}$, but not both. In order to distinguish between these two possibilities, the recombination energy of the species thought to be $TMM^{\bullet+}$ and the ionization energy of MCP were determined.

The adiabatic recombination energy of the radical cation expected to be $TMM^{\bullet+}$ was bracketed by allowing it to react with a series of neutral reagents of known ionization energies and monitoring products corresponding to electron transfer (Table 1). The ion does not abstract an electron from cyclopentanone (IE 9.25 eV[16]) or molecules with ionization energies greater than 9.25 eV; however, electron abstraction occurs from 1,4-dioxane (IE 9.19 eV[16]) and reagents with lower ionization energies than 9.19 eV. These findings indicate that the adiabatic recombination energy of $TMM^{\bullet+}$ is 9.2 ± 0.1 eV.

The adiabatic ionization energy of methylenecyclopropane was determined by examining its reactions with a number of radical cations of known recombination energies and noting the formation of $C_4H_6^{\bullet+}$ (Table 2). Tetrahydrofuran radical cation (RE 9.38 eV[16]) does not react with MCP, and the same applies to all radical cations studied with a recombination energy less than 9.38 eV. However, formation of $C_4H_6^{\bullet+}$ was observed for the methanethiol radical cation (RE 9.44 eV[16]) and radical cations with recombination energies greater than 9.44 eV. On the basis of these findings, the adiabatic ionization energy of MCP is concluded to be 9.4 ± 0.1 eV. This ionization energy is consistent with the previously estimated value of <9.57 eV.[16]

TABLE 2: Reactions between Methylenecyclopropane and Selected Radical Cations of Known Recombination Energy

ion	recombination energy (eV)[a]	result
$acetone^{\bullet+}$	9.705 ± 0.005	+[b]
$iodomethane^{\bullet+}$	9.54 ± 0.05	+
$methanethiol^{\bullet+}$	9.4386 ± 0.05	+
$tetrahydrofuran^{\bullet+}$	9.38 ± 0.05	−[c]
$3\text{-pentanone}^{\bullet+}$	9.31 ± 0.01	−
$allyl\ iodide^{\bullet+}$	9.298	−
$cyclopentanone^{\bullet+}$	9.25 ± 0.02	−
$1,4\text{-dioxane}^{\bullet+}$	9.19 ± 0.02	−
$bromobenzene^{\bullet+}$	9.00 ± 0.02	−

[a] Reference 16. [b] Electron transfer was observed as the major reaction channel. [c] Fast reactions other than electron transfer were observed.

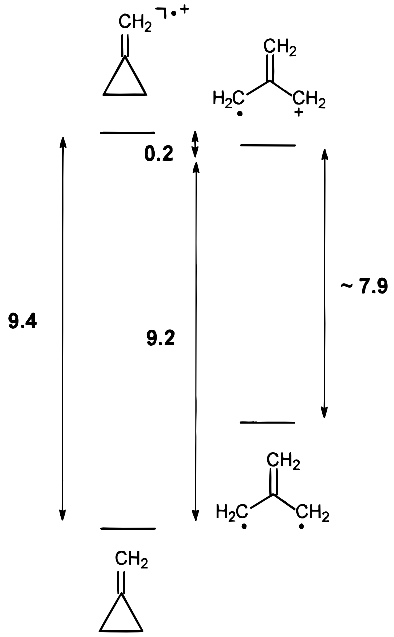
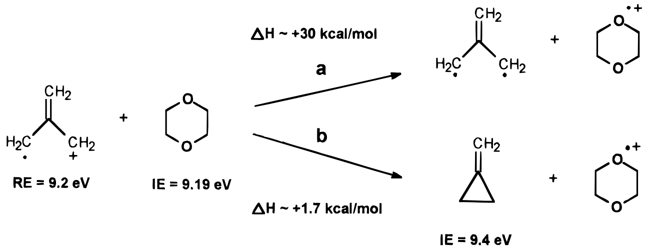


Figure 1. Relative energies of TMM (**1**), MCP, and their radical cations **2** and **5**.

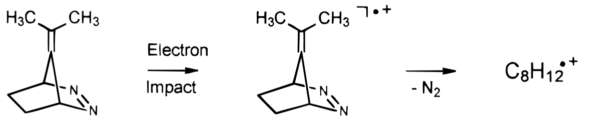
The recombination energy of the ion assumed to correspond to $TMM^{\bullet+}$ differs by 0.2 eV from the ionization energy of MCP. Hence, the atom connectivity of the ion and MCP is likely to be different. The reactant ion population is concluded to consist of isomerically pure $TMM^{\bullet+}$, as initially assumed. This conclusion presents a dilemma, however, since the recombination energy measured for $TMM^{\bullet+}$ (9.2 eV) is drastically different from what one would expect, based on the ionization energies of allyl radicals (e.g., 2-methylenepropene, **6**: IE 7.9 eV[16]) and the recombination energy measured for another TMM-type radical cation, **7** (7.41 ± 0.05 eV).[9c] The electron transfer reactions of $TMM^{\bullet+}$ seem to have a significantly greater thermodynamic driving force than would be associated with the simple production of TMM. However, the large recombination energy of $TMM^{\bullet+}$ is readily rationalized if the electron transfer reactions yield MCP, and not TMM, as the final neutral product. This process would lead to a recombination energy for $TMM^{\bullet+}$ that is almost as great as that of $MCP^{\bullet+}$ (equal to the ionization energy of MCP, 9.4 eV) since the difference between these two recombination energies would correspond to the relatively small stability difference between $TMM^{\bullet+}$ and $MCP^{\bullet+}$ (Figure 1). The stability difference has been calculated by Du and Borden to be 6.5 kcal mol^{-1}.[11] This value is in an excellent agreement with the difference between the two recombination energies (0.2 eV = 5 kcal mol^{-1}).

The above considerations are illustrated in Scheme 3 for 1,4-dioxane, the reagent with the greatest ionization energy that is still able to reduce $TMM^{\bullet+}$. Assuming that the ionization energy of TMM is about 7.9 eV, as expected based on the ionization

SCHEME 3



SCHEME 4



energy of 2-methylene propene (**6**: IE 7.9 eV[16]), electron transfer from 1,4-dioxane to produce TMM would be prohibitively endothermic (30 kcal mol^{-1}) and cannot occur in the experiments discussed here. Production of MCP, however, is feasible since this reaction is nearly thermoneutral ($\Delta H = +1.7$ kcal mol^{-1}).

2-Isopropylidenecyclopentane-1,3-diyl Radical Cation. A $TMM^{\bullet +}$ derivative (**9**), the radical cation of 2-isopropylidenecyclopentane-1,3-diyl, has been produced previously in solution via photochemical deazetation of a charge transfer complex between 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene and tetracyanoethylene.[10] Another route to this radical cation involves dissociative electron ionization of 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (Scheme 4). This approach was employed here to generate **9** for the examination of its reactivity in the gas phase. The results obtained are shown in Table 3.

As discussed above for $TMM^{\bullet +}$, the observed electron transfer reactions allow bracketing of the recombination energy of **9** to be 7.8 ± 0.1 eV. However, the product formed upon reduction of **9** is not entirely certain at this time. This reduction could yield either 2-isopropylidenecyclopentane-1,3-diyl triplet or the strained closed-shell isomer, 5-isopropylidenebicyclo[2.1.0]-pentane. Both are of comparable energy, about 13−15 kcal mol^{-1} lower than that of 2-isopropylidenecyclopentane-1,3-diyl singlet.[20] In any event, the recombination energy of 7.8 ± 0.1 eV for **9** is a good estimate for the ionization energy of 2-isopropylidenecyclopentane-1,3-diyl triplet biradical. This value is close to the ionization energy of the related allyl radical, 2-methylenepropene (7.9 eV[16]), and the recombination energy of the 1,1-diphenyl derivative **7** (7.41 ± 0.05 eV).[9c]

The $TMM^{\bullet +}$ derivative **9** was found to be very unreactive (Table 3). In sharp contrast to $TMM^{\bullet +}$, this ion does not react with dimethyl disulfide, dimethyl diselenide, or benzeneselenol. In fact, the only reagents that yield observable products are di-*tert*-butyl disulfide, triethylamine, and *N*,*N*-dimethylaniline. Slow electron and/or hydrogen atom abstraction and/or proton transfer reactions were observed for these three reagents (Table 3).

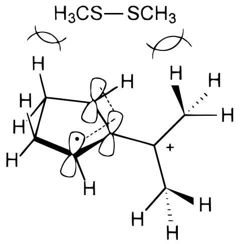
The reactivity differences between the $TMM^{\bullet +}$ derivative **9** and $TMM^{\bullet +}$ may be partially attributed to structural factors, such as alkyl substitution, that stabilize the odd spin and charge in the bigger ion relative to $TMM^{\bullet +}$, and hence reduce the thermodynamic driving force for its reactions. Steric factors are also likely to play a role. It has been previously shown that the diphenyl $TMM^{\bullet +}$ derivative **7** adopts a bisected conformation (spin density concentrated in the propylene moiety, the charge delocalized over the diarylmethylene group).[21] If the $TMM^{\bullet +}$ derivative **9** possesses a similar bisected structure or even a slightly twisted one, the approach of CH_3SSCH_3 would be hindered by steric repulsion from the methyl groups and the ring methylene hydrogen atoms (Scheme 5).

TABLE 3: Reaction Products, Their Branching Ratios, and the Efficiencies of the Reactions of the 2-Isopropylidenecyclopentane-1,3-diyl Radical Cation with Selected Neutral Reagents

neutral reagent	ionization energy[a] (eV)	products	efficiency[b]
dimethyl disulfide	8.1 ± 0.1[c]	no reaction	
benzeneselenol	8.0 ± 0.1[d]	no reaction	
dimethyl diselenide	7.9 ± 0.1[e]	no reaction	
di-*tert*-butyl disulfide	7.7	$C_8H_{18}S_2^{\bullet +}$ (80%) $C_8H_{13}^{+}$ (20%)	0.4
triethylamine	7.50 ± 0.02	$(C_2H_5)_3N^{\bullet +}$ (80%) $(C_2H_5)_3NH^{+}$ (20%)	0.9
N,*N*-dimethylaniline	7.12 ± 0.02	$C_6H_5N(CH_3)_2^{\bullet +}$ (100%)	0.9

[a] Reference 16. [b] Reaction efficiencies are given by k_{exp}/k_{coll}. [c] Reference 17b. [d] Reference 19a. [e] Reference 18.

SCHEME 5



Conclusions

The trimethylenemethane radical cation and its derivative, the 2-isopropylidenecyclopentane-1,3-diyl radical cation, are readily produced in the gas phase by electron ionization of methylenecyclopropane and by dissociative electron ionization of 7-isopropylidene-2,3-diazabicyclo-[2.2.1]hept-2-ene. The two radical cations exhibit dramatic reactivity differences. The sterically hindered 2-isopropylidenecyclopentane-1,3-diyl radical cation is unreactive toward most reagents studied. However, the ion is neutralized via electron transfer by molecules with ionization energies lower than 7.8 eV, indicating that the recombination energy of this radical cation (and thus, the ionization energy of the 2-isopropylidenecyclopentane-1,3-diyl biradical) is 7.8 ± 0.1 eV. This value is in a good agreement with the expectations for such a $TMM^{\bullet +}$ derivative (7.4−7.9 eV). In sharp contrast to the 2-isopropylidenecyclopentane-1,3-diyl radical cation, $TMM^{\bullet +}$ reacts with dimethyl disulfide, dimethyl diselenide, and benzeneselenol via typical radical pathways, i.e., thiomethyl, selenomethyl, and hydrogen atom abstraction, respectively. Unexpectedly, a fast electron transfer was found to accompany these reactions. The strong preference of $TMM^{\bullet +}$ to undergo electron abstraction is rationalized by production of methylenecyclopropane (and not TMM) as the final neutral product.

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