

Gas-Phase Reactivity of Charged  $\pi$ -Type Biradicals

Shane E. Tichy, Eric D. Nelson, F. Sedinam Amegayibor, and Hilikka I. Kenttämäa\*

*Contribution from the Department of Chemistry, Purdue University,  
West Lafayette, Indiana 47907-2084*

Received January 26, 2004; E-mail: hilikka@purdue.edu

**Abstract:** Four  $\pi,\pi$ -biradicals, 2,6-dimethylenepyridinium and the novel isomers *N*-(3-methylenephenyl)-3-methylenepyridinium, *N*-phenyl-3,5-dimethylenepyridinium, and *N*-(3,5-dimethylenephenyl)pyridinium ions, were generated and structurally characterized in a Fourier transform ion cyclotron resonance mass spectrometer. Their gas-phase reactivity toward various reagents was compared to that of the corresponding monoradicals, 2-methylenepyridinium, *N*-phenyl-3-methylenepyridinium, and *N*-(3-methylenephenyl)pyridinium ions. The biradicals reactivity was found to reflect their predicted multiplicity. The 2,6-dimethylenepyridinium ion, the only biradical in this study predicted to have a closed-shell singlet ground state, reacts significantly faster than the other biradicals, which are predicted to have triplet ground states. In fact, this biradical reacts at a higher rate than the analogous monoradical, which suggests that to avoid the costly uncoupling of its unpaired electrons, the biradical favors ionic mechanisms over barriered radical pathways. In contrast, the second-order reaction rate constants of the isomeric biradicals with triplet ground states are well approximated by those of the analogous monoradicals, although the final reaction products are sometimes different. This difference arises from rapid radical-radical recombination of the initial monoradical reaction products. The overall reactivity toward the hydrogen-atom donors benzeneselenol and tributylgermanium hydride is significantly greater for the radicals with the charged site in the same ring system as the radical site. This finding indicates that polar effects play an important role in controlling the reactivity of  $\pi,\pi$ -biradicals, just as has been demonstrated for  $\sigma,\sigma$ -biradicals.

## Introduction

Organic biradicals are thought to exist as short-lived intermediates in various photochemical and thermal reactions.<sup>1–3</sup> Recently, there has been a resurgence in the study of biradicals for potential use in materials science.<sup>4–6</sup> Investigators have begun to examine the utility of biradicals as unique building blocks for advanced materials with specific magnetic, electrical, or optical characteristics.<sup>7–10</sup> Particularly, non-Kekulé molecules (e.g., *m*-xylylene, trimethylenemethane, 2,4-dimethylenecyclobutane-1,3-diyl, and 1,3-cyclopentenediyl) with fully delocalized  $\pi$ -systems have attracted significant attention as models for ferromagnetic coupling in high-spin organic polymers.<sup>10–13</sup>

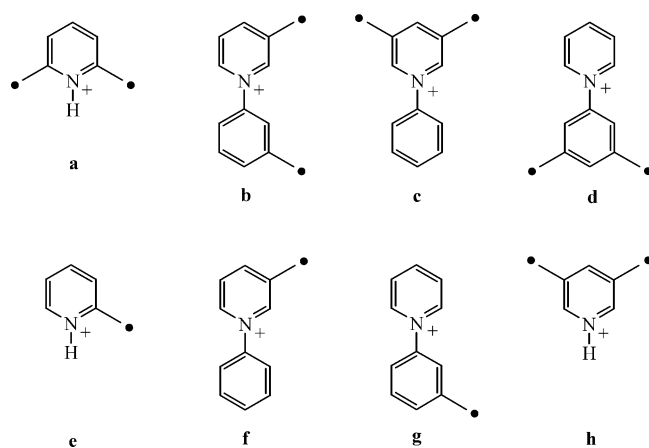
A biradical's reactivity is expected to be influenced by its ground-state spin multiplicity. Hence, extensive research has been dedicated to the determination of the ground-state spin preferences of these species.<sup>5,13–21</sup> A triplet biradical is likely

to react similarly to its monoradical counterpart.<sup>20,22–25</sup> On the other hand, some singlet biradicals have been found to be less-reactive radicals than their monoradical counterparts. For example, *ortho*-benzynes ( $\Delta E_{ST} = 37.5$  kcal/mol)<sup>26</sup> does not display any radical reactivity and undergoes exclusively nucleophilic or electrophilic addition reactions.<sup>27–31</sup> Even when there is only a slight preference for the singlet ground state (e.g., 9,10-didehydroanthracene,  $\Delta E_{ST} \approx 3.8$  kcal/mol), hydrogen abstraction reactions can be 100–200 times slower than for comparable monoradicals (9-dehydroanthracene).<sup>32–36</sup> Chen and

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Scheme 1



co-workers<sup>33–35</sup> rationalized this finding based on the necessity to uncouple a singlet biradical's electrons in the transition state of these reactions. They proposed that part of the  $\Delta E_{ST}$  ends up as an increment to the energy of the transition state, thus hindering radical reactions. A recent computational study by Clark and Davidson<sup>36</sup> is in general agreement, although a less-strong dependence between the  $\Delta E_{ST}$  of the biradical and the transition-state energy for H-atom abstraction is proposed (the difference in energy between the ground state and first excited singlet state of the biradical/substrate complex is thought to be the critical variable). In any case, the reactivity of biradicals with no strong preference for either multiplicity ( $\Delta E_{ST} \approx 0$ ) might be expected to approach that of analogous monoradicals. The reactivity of some non-Kekulé molecules has been probed in solution in an attempt to deduce the spin states of the reactive species.<sup>24</sup> However, the current understanding of the factors that control the reactivity of these species is limited.

Recently, we used mass spectrometry to examine the gas-phase reactivity of two *meta*-xylylene derivatives, the 2,6- and 3,5-dimethylenepyridinium ions,<sup>38</sup> predicted to have a closed-shell singlet ( $\Delta E_{ST} = -2.4$  kcal/mol) and a triplet ground state ( $\Delta E_{ST} = 6.4$  kcal/mol), respectively.<sup>39</sup> The two biradicals were found to display reactivity that is different and appears to reflect their calculated spin states. For example, the 3,5-dimethylenepyridinium ion was found to react via radical pathways and sequentially abstract two hydrogen atoms from benzeneselenol. In contrast, the 2,6-dimethylenepyridinium ion appears to react via electrophilic pathways to form addition products. To further explore the factors that influence the reactivity of fully delocalized  $\pi$ -type biradicals, we have carried out a detailed study on the intrinsic reactivity of the 2,6-dimethylenepyridinium ion (**a**), the *N*-(3-methylenephényl)-3-methylenepyridinium ion (**b**), the *N*-phenyl-3,5-dimethylenepyridinium ion (**c**), and the *N*-(3,5-dimethylenephényl)pyridinium ion (**d**), as well as some related monoradicals (Scheme 1).

## Experimental Section

All experiments were carried out using an Extrel model FTMS 2001 Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR).

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This instrument, described previously,<sup>38,40–42</sup> contains a differentially pumped dual cell placed within the magnetic field produced by a 3.0 T superconducting magnet operated at ca. 2.7 T. The two cells are separated by a common plate (the conductance limit) that has a 2-mm hole in the center. This plate and the other two trapping plates were kept at +2 V unless otherwise stated. The nominal base pressure in each cell ( $<1 \times 10^{-9}$  Torr) was maintained by a turbomolecular pump (330 L/s), backed with a mechanical pump.

The charged radicals and biradicals were generated using a procedure reported earlier.<sup>38,40–42</sup> Some specific details are given below.

Generation of the biradical **a** involved protonation of a bis(bromomethyl)pyridine precursor via methanol chemical ionization. The substituted 2,6-bis(bromomethyl)pyridine was introduced at a nominal pressure of  $4.0 \times 10^{-8}$  Torr into one side of the dual cell of the FT-ICR through a Varian leak valve. Methanol was added at approximately the same nominal pressure into the same cell through a batch inlet system equipped with a variable leak valve. The mixture was subjected to electron ionization (typically 15-eV electron energy, 5- $\mu$ A emission current, and 50-ms ionization time) and allowed to react for approximately 2 s, which resulted in an abundant signal for the protonated pyridine molecules.

The protonated pyridine molecules, generated in one side of the dual cell as described above, were transferred into the other cell by grounding the conductance limit plate for approximately 140  $\mu$ s. To maximize transfer efficiency, the technique of quadrupolar axialization<sup>43</sup> was applied prior to transfer to refocus the ion population's cyclotron radius along the magnetic field axis. The transferred ions were allowed to cool for 2 s by IR emission and by collisions with the neutral molecules present in this cell (the reagent to be used in the final stage of the experiment). Sustained off-resonance irradiated collision-activated dissociation<sup>44</sup> (SORI-CAD) was employed to accomplish carbon–bromine bond cleavage. The SORI-CAD was implemented by introducing argon via a pulsed valve assembly<sup>45</sup> (the nominal peak pressure in the cell was approximately  $1 \times 10^{-5}$  Torr) and collisionally activating the ions with argon for 200 ms by using a slightly ( $\sim 1$  kHz) off-resonant rf potential to kinetically excite the ion population.<sup>44</sup> This process was used to generate the monoradical 2-bromomethyl-6-methylenepyridinium ion. A second SORI-CAD event (200 ms at a frequency 1.0 kHz higher than the frequency of the precursor ion) caused the other carbon–bromine bond to be homolytically cleaved, producing biradical **a**.

Biradicals **b**, **c**, and **d** were synthesized by using a variation of the procedure described above. A pyridine precursor (3-picolyl bromide for **b**, 3,5-bis(bromomethyl)pyridine for **c**, or pyridine for **d**) was introduced at a nominal pressure of  $4.0 \times 10^{-8}$  Torr into one side of the dual cell through a Varian leak valve. A halobenzene (3-bromobenzyl chloride for **b**, chlorobenzene for **c**, or 3,5-bis(bromomethyl)chlorobenzene for **d**), was introduced at a nominal pressure of  $6.0 \times 10^{-8}$  Torr into the same cell through a batch inlet system equipped with a variable leak valve. The mixture was subjected to electron ionization, which resulted in an intense signal for halobenzene radical cations. These ions were allowed to react with the neutral pyridine derivative present in the cell, leading to ipso-substitution<sup>46,47</sup> of the chlorine atom. Formation of an abundant halogen displacement product occurred in 5 s. This product was transferred into the other cell and subsequently subjected to multiple SORI-CAD events, which induced homolytic cleavage of the carbon–bromine bonds to yield the  $\pi$ -type biradicals **b**, **c**, and **d**.

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The biradicals were isolated by ejecting all unwanted ions from the cell through the application of stored-waveform inverse Fourier transform (SWIFT) excitation pulses<sup>48,49</sup> to the cell plates. They were then allowed to react with various neutral reagents for variable periods of time (typically 0.1–50 s). The ions were excited for detection by using “chirp” excitation. All spectra were collected as 64k data points and as an average of at least 10 transients, and subjected to one zero-flier prior to Fourier transformation.

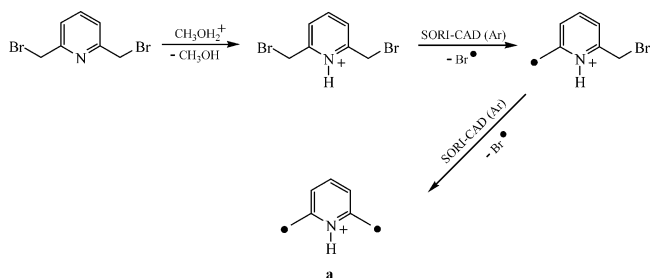
The concentration of the neutral reagent is much greater than that of the ion in the cell. Hence, the reactions studied here follow pseudo first-order kinetics. The second-order rate constant ( $k_{\text{exp}}$ ) of each ion–molecule reaction was obtained from a semilogarithmic plot of the relative abundance of the reactant ion versus time. Collision rate constants ( $k_{\text{coll}}$ ) were calculated using the parameterized trajectory theory of Su et al.<sup>50</sup> The reaction efficiencies are given as  $k_{\text{exp}}/k_{\text{coll}}$ . The accuracy of rate constant measurements is estimated to be  $\pm 50\%$ , whereas the precision was usually better than  $\pm 10\%$ . The pressure readings of the ion gauges were corrected for the sensitivity of the ion gauge toward each neutral reagent<sup>51</sup> and the pressure gradient between the cell and the ion gauge. The latter correction factor was obtained for each neutral reagent by measuring its rates of exothermic proton abstraction from protonated ethanol and electron-transfer to ionized carbon disulfide (assumed to occur at collision rate).

All calculations were performed using the Gaussian 98 Revision A.9 computational software package.<sup>52</sup> Molecular geometries of all species were optimized using either the 6-311+G(d,p) or the correlation-consistent polarized valence-double- $\zeta$  (cc-pVDZ) basis set. All geometries were confirmed to be local minima by computation of analytical vibrational frequencies (no imaginary frequencies for geometry minima, one imaginary frequency for transition states). These frequencies were also used to compute zero-point vibrational energies (ZPVE) as well as thermal corrections to all enthalpy values. The BPW91 analytical frequencies were scaled by 0.9774.<sup>53</sup>

## Results and Discussion

**Synthesis and Structural Characterization.** The biradicals (**a–d**, Scheme 1) were generated employing a multistep synthesis procedure shown in Schemes 2 and 3. Our previous work has demonstrated that sustained off-resonance irradiated collision-activated dissociation<sup>44</sup> (SORI–CAD), employed here to effect bond cleavage, can be used to generate stable aromatic biradicals. For example, we have shown that charged derivatives of *m*-benzynes<sup>54,55</sup> and *p*-benzynes<sup>32</sup> are generated without isomerization by using multiple SORI–CAD events to cause homolytic cleavages of bromine atoms, iodine atoms, and nitro groups from a phenyl ring. For the systems studied here, a

**Scheme 2**



benzyl–halogen bond is broken during the SORI–CAD event to form a  $\pi$ -radical (Schemes 2 and 3). This bond is weaker than the  $\sigma$ -bond broken upon formation of the benzenes. However, the benzyl radicals have access to isomerization pathways that are not available to their  $\sigma$ -radical counterparts. Therefore, the structures of the ions formed by SORI–CAD were examined both experimentally and computationally.

Previously, it has been shown that  $\sigma$ -type radicals with a spatially separate charge (a subgroup of distonic radical cations) react exclusively by thiomethyl- and iodo-abstraction with dimethyl disulfide and allyl iodide, respectively.<sup>40,41,56–58</sup> However,  $\cdot\text{SCH}_3$  and  $\cdot\text{I}$  abstraction from dimethyl disulfide and allyl iodide by the benzyl radical is endothermic by 3.8 and 4.2 kcal/mol, respectively.<sup>22,59–61</sup> Therefore, it was not unexpected that the benzyl radicals studied in this work were found to be unreactive toward these substrates. It is inferred that the  $\pi$ -type monoradicals and biradicals do not undergo isomerization to a  $\sigma$ -radical during the SORI–CAD event. However, several other structural isomers (Scheme 4) must be considered that may arise through other rearrangement pathways. Especially important are those that lie lower in energy than the desirable charged biradicals.

Calculations at the BPW91/aug-cc-pVDZ + ZPVE level of theory predict that triplet phenyl carbene ion isomers of **c** and **d**, such as **i** and **j** (Scheme 4), lie higher in energy than **c** and **d** by 31 and 36 kcal/mol, respectively. Hence, these ions were not considered further. However, calculations at the same level of theory predict the ring-expanded ion **k** (Scheme 4) and rearranged ion **l** (Scheme 4) to lie lower in energy than the isomeric charged biradical **a** by approximately 7 kcal/mol. The rearrangement of biradical **a** to form the ring-expanded isomer **k** or the 6-methyl-2-methylenepyridine cation **l** must involve a transfer of a hydrogen atom or proton to one of the methylene groups from the nitrogen. These isomerization processes would make the acidic proton indistinguishable from the carbon-bound hydrogens. To examine whether this takes place, the nitrogen-deuterated form of biradical **a** was allowed to react with the strong base triethylamine. The observed exclusive deuterium transfer to triethylamine from the deuterated form of **a** conclusively demonstrates that the biradical has not rearranged to **k** or **l**.

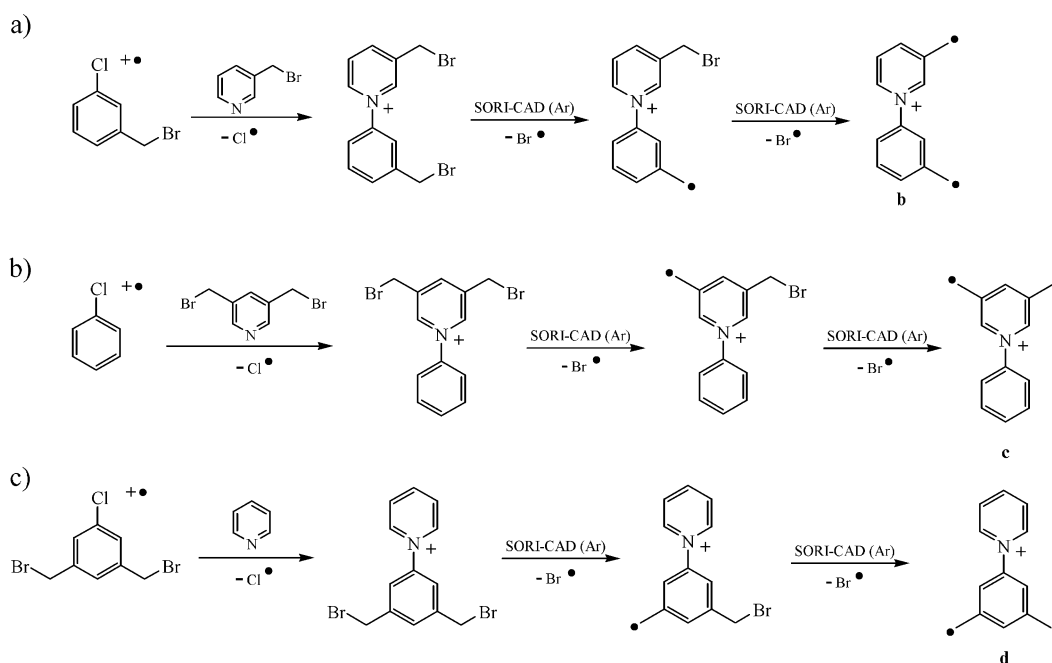
Charged monoradicals **f** and **g** exclusively abstract a hydrogen atom when allowed to react with benzeneselenol. Therefore,

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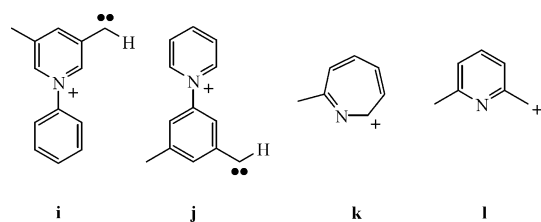
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Scheme 3



Scheme 4



biradicals **a**, **b**, **c**, and **d** may be expected to abstract two hydrogen atoms (and possibly form an addition product via an initial hydrogen-atom abstraction followed by a radical–radical recombination of the selenophenyl radical and the other reactive site). Indeed, when the biradicals were allowed to react with benzeneselenol, two sequential hydrogen-atom abstractions, as well as a stable addition product, were observed (Figures 1a and b, 2a and b).

Further evidence that biradicals **a**, **b**, **c**, and **d** are produced intact without subsequent isomerization is the observation of the linear decay of the natural logarithm of the abundance of the biradical reactant ions as a function of time. This finding suggests that the reactant ion population only contains one isomer. In addition, in the reactions with the neutral reagents studied, reproducible and different reaction efficiencies ( $k_{\text{exp}}/k_{\text{coll}}$ ) were measured for the different biradicals, again suggesting that they are distinct species.

**Electronic Ground States of the Biradicals.** The biradical *m*-xylylene is a non-Kekulé molecule that is known to exhibit substantial preference for the triplet ground state ( $\Delta E_{\text{ST}} = 9.6$  kcal/mol).<sup>21</sup> West et al.<sup>39</sup> have predicted, based on molecular orbital calculations, that the electronic ground state of *m*-xylylene (Figure 3) can be perturbed by the introduction of a positively charged group into the high-spin system. Their calculations suggest that substituting a CH group with an electronegative  $\text{NH}^+$  group at a position with a large coefficient in one of the NBMOs, along with a small one in the other NBMO, opens up the HOMO–LUMO energy gap. Since one NBMO is stabilized relative to the other, the singlet ground

state is preferred. Indeed, calculations by West et al.<sup>39</sup> predict **a** to be a ground-state singlet by 2.4 kcal/mol. However, the isomeric 3,5-dimethylenepyridinium ion (**h**, Scheme 1) with a  $\text{NH}^+$  group at a node is calculated to be a ground-state triplet by 6.4 kcal/mol.<sup>39</sup> Based on these findings, one may expect the charged biradicals **c** and **d** to have a singlet–triplet splitting between 6.4 and 9.6 kcal/mol.

Charged biradical **b** is an especially interesting species, given that the two radical sites are separated by a nonplanar biphenyl ring system (Figure 4). This nonplanarity, in addition to the large distance between the two radical sites, should result in a small singlet–triplet gap. Calculations at the CCSD(T)/6-31G(d)//BPW91/6-31G(d) level of theory predict the  $\Delta E_{\text{ST}}$  to be 0.21 kcal/mol. As a result, **b** may be regarded as a biradical with essentially no preference for either the singlet or triplet state ( $\Delta E_{\text{ST}} \approx 0$ ).

**Reactions with Tributylgermanium Hydride, *tert*-Butyl Isocyanide, and Benzeneselenol.** Biradicals **b**, **c**, and **d** undergo addition to, and abstract a H-atom from, the hydrogen donors benzeneselenol<sup>40,42,62–67</sup> and tributylgermanium hydride,<sup>68</sup> whereas the analogous monoradicals **f** and **g** react with these reagents by exclusive H-atom abstraction. The lack of addition of the monoradicals is explained by the presence of only one radical site in these species. The biradicals have two reactive sites, which makes further reactions possible within the collision complex after hydrogen-atom transfer. An addition product is likely observed when the neutral radical product does not escape the collision complex, but instead reacts with the remaining radical site of the former biradical by radical–radical recombination (Scheme 5). On the other hand, if the neutral radical

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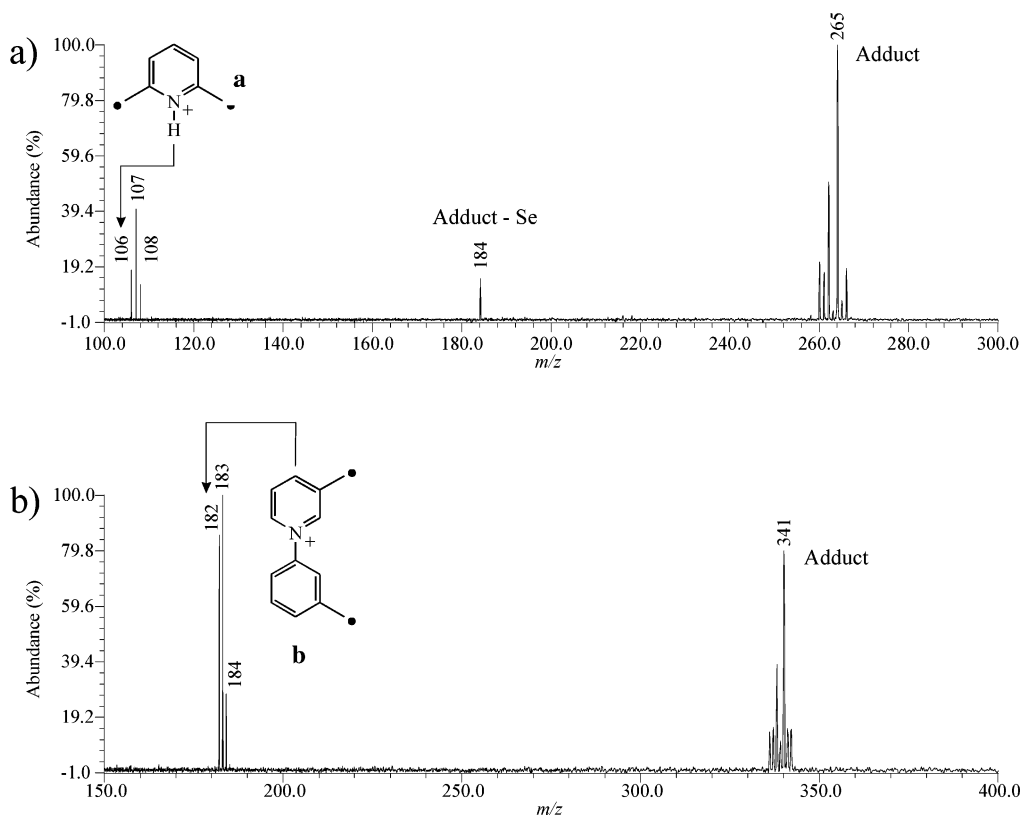
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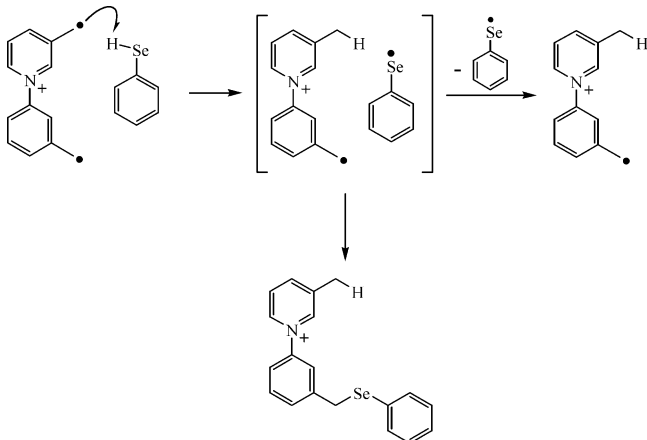
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**Figure 1.** Reaction of **a** ( $m/z$  106) (a) and **b** ( $m/z$  182) (b) with benzeneselenol for 10 and 45 s, respectively (nominal pressure  $3.0 \times 10^{-7}$  Torr).

#### Scheme 5

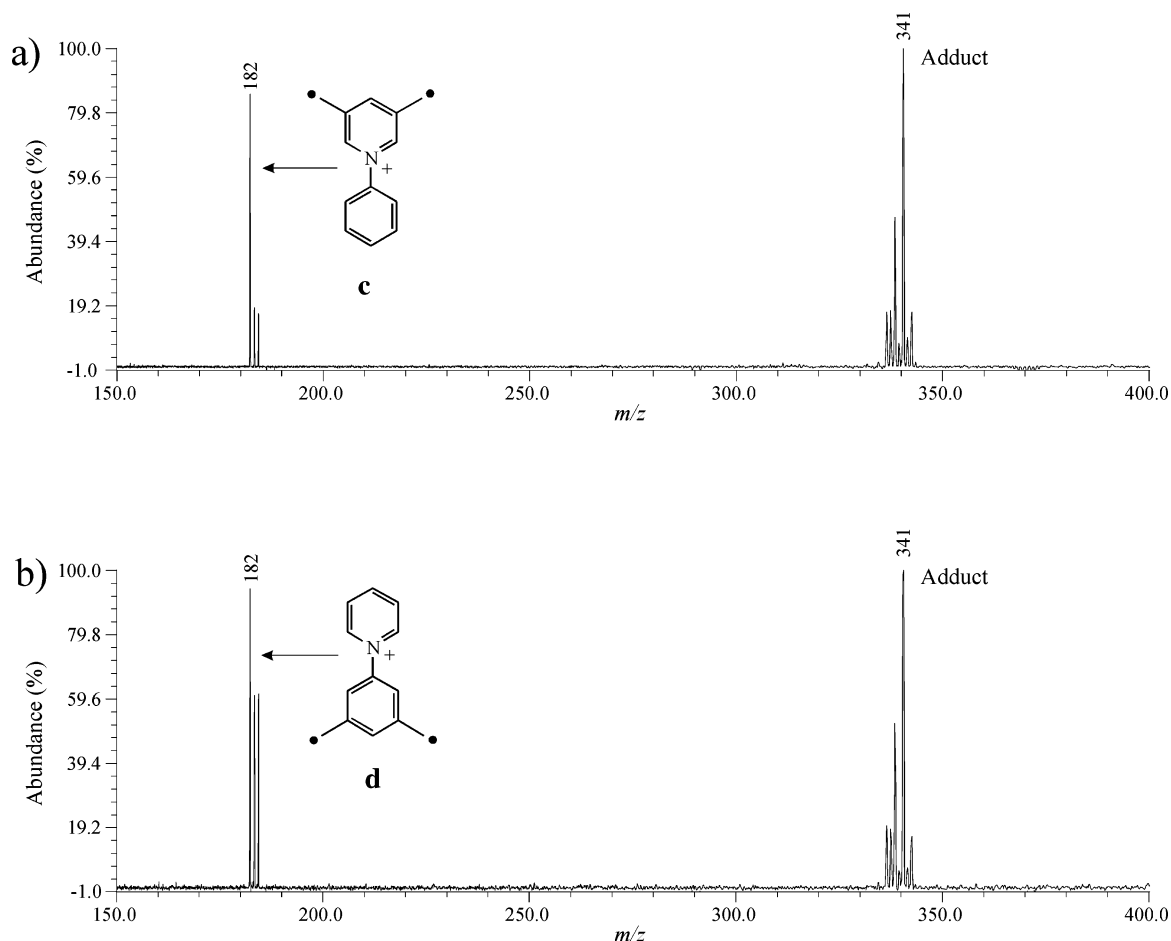


escapes the collision complex, the remaining charged monoradical can react with another H-atom donor molecule by hydrogen-atom abstraction. In support of the above proposal, the prevalence of the addition product appears to depend on the distance between the methylene radical moieties in the biradicals. Addition dominates (branching ratio  $\geq 70\%$ ) the reaction of the biradicals **c** and **d** where the radical sites are approximately  $5 \text{ \AA}$  apart (Figure 4). However, H-atom abstraction is the dominant pathway (branching ratio  $\geq 40\%$ ) for biradical **b**, whose methylene groups are approximately  $2.5 \text{ \AA}$  further apart than in **c** and **d** (Figure 4). The rate-determining step for both reactions is likely the H-atom abstraction step. In fact, the rates of reaction of these biradicals with benzeneselenol and tributylgermanium hydride are well approximated by the reaction rates of the monoradical analogues (e.g., biradicals **c** and **d** react at a similar rate as monoradicals **f** and **g**,

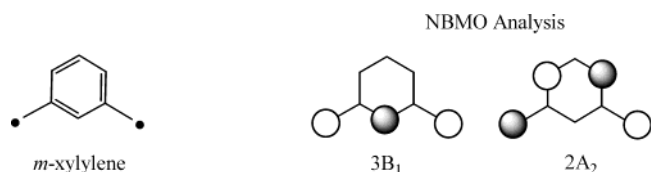
respectively). Biradical **b** contains two different radical sites, one related to the monoradical **f** and the other to **g**. The reactivity of **b** is nearly identical to that of **f**, the more reactive of the two monoradicals. For example, monoradical **f** and biradicals **b** and **c** abstract a H-atom from tributylgermanium hydride at an efficiency of approximately 10%, while the monoradical **g** and biradical **d** undergo the same reaction at an efficiency of less than 1%. Further, **f**, **b**, and **c** abstract a hydrogen atom from benzeneselenol at an efficiency of approximately 1%, while **g** and **d** undergo the same reaction at an efficiency of 0.3%. Hence, the observed reactivity ordering for these species is **b**  $\approx$  **c**  $\approx$  **f**  $>$  **d**  $\approx$  **g**.

Biradical **a** was found to possess remarkably different chemical properties from the other three biradicals. Most importantly, **a** is highly reactive toward all reagents studied, while **b**, **c**, and **d** usually react slowly or not at all. For example, **a** reacts with *tert*-butyl isocyanide predominantly via HCN abstraction at an efficiency of 27%, while **b**, **c**, and **d** were found to be unreactive toward this reagent (i.e., no reaction was observed within our detection limits; efficiency  $< 0.001\%$ ) (Tables 1 and 2). Biradical **a** also displays unique reactivity toward tributylgermanium hydride. While **b**, **c**, and **d** add to and abstract hydrogen atoms from tributylgermanium hydride at efficiencies of 11%, 10%, and 0.6%, respectively, **a** rapidly (efficiency = 80%) forms a product that is consistent with addition followed by loss of butane (Figure 5).

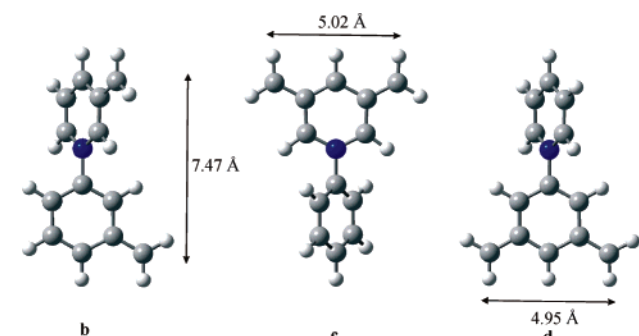
The exceptionally high reactivity observed for **a**, as compared to the other biradicals, may at first glance appear to be in disagreement with the predicted<sup>39</sup> closed-shell singlet ground state. Indeed, **a** reacts faster than even the analogous monoradical **e**. This, and the fact that **a** does not yield radical products, may be explained by different reaction mechanisms for **a** and



**Figure 2.** Reaction of **c** ( $m/z$  182) (a) and **d** ( $m/z$  182) (b) with benzeneselenol for 45 and 200 s respectively (nominal pressure  $3.0 \times 10^{-7}$  Torr).



**Figure 3.** Schematic representations of the Hückel nonbonding molecular orbitals (NBMO) of *m*-xylylene.

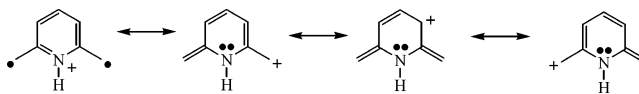


**Figure 4.** Optimized structures of **b**, **c**, and **d** as calculated at the UBPW91/6-311+G(d,p) level of theory. The distance between the methylene groups (in angstroms) is indicated for each biradical.

**e.** Consideration of the valence bond description of the singlet biradical **a** (Scheme 6) suggests that this biradical may be able to react via near-barrierless ionic pathways in competition with barriered radical pathways.

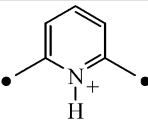
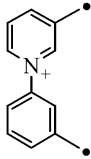
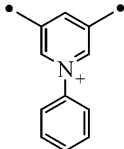
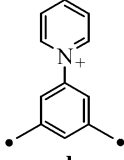
For example, the unique product formed upon interaction of the biradical **a** with tributylgermanium hydride (addition fol-

#### Scheme 6

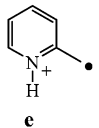
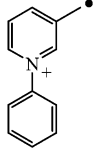
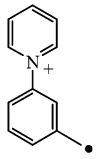


lowed by loss of  $C_4H_{10}$ ) can be explained by an ionic pathway that is initiated by hydride abstraction to produce the tributylgermanyl cation. The tributylgermanyl cation then adds to the methylene site or some other unsaturated carbon to form an adduct, which finally undergoes a 1,2-elimination of butane (Scheme 7). Similarly, the unique HCN abstraction reaction observed upon interaction of **a** with *tert*-butyl isocyanide almost certainly follows an ionic pathway, since biradicals **b**, **c**, and **d** and the monoradicals **f** and **g** are unreactive toward this reagent. In our previous study<sup>38</sup> of the reactivity of **a**, we proposed a mechanism for this reaction in which cyanide abstraction produces the *tert*-butyl cation that transfers a proton to yield the observed HCN abstraction product. The analogous monoradical **e** was found to react almost three orders of magnitude slower than **a** (efficiency = 0.04%), and it reacts by typical radical pathways (i.e., addition (55%) and H-atom abstraction (45%)). Since monoradicals **f** and **g** failed to react with this reagent (within our detection limits; efficiency < 0.001%), the nitrogen-bound proton of monoradical **e** may be involved in enhancing the reactivity of this radical toward *tert*-butyl isocyanide. In summary, the reactivity of **a**, as compared to **e**, is in agreement with the singlet electronic ground-state assigned for this biradical.

**Table 1.** Reactions Observed for Biradicals **a–d** (Relative Product Abundances Given in Parentheses) and Their Efficiencies (Eff. =  $k_{\text{exp}}/k_{\text{coll}}$ )

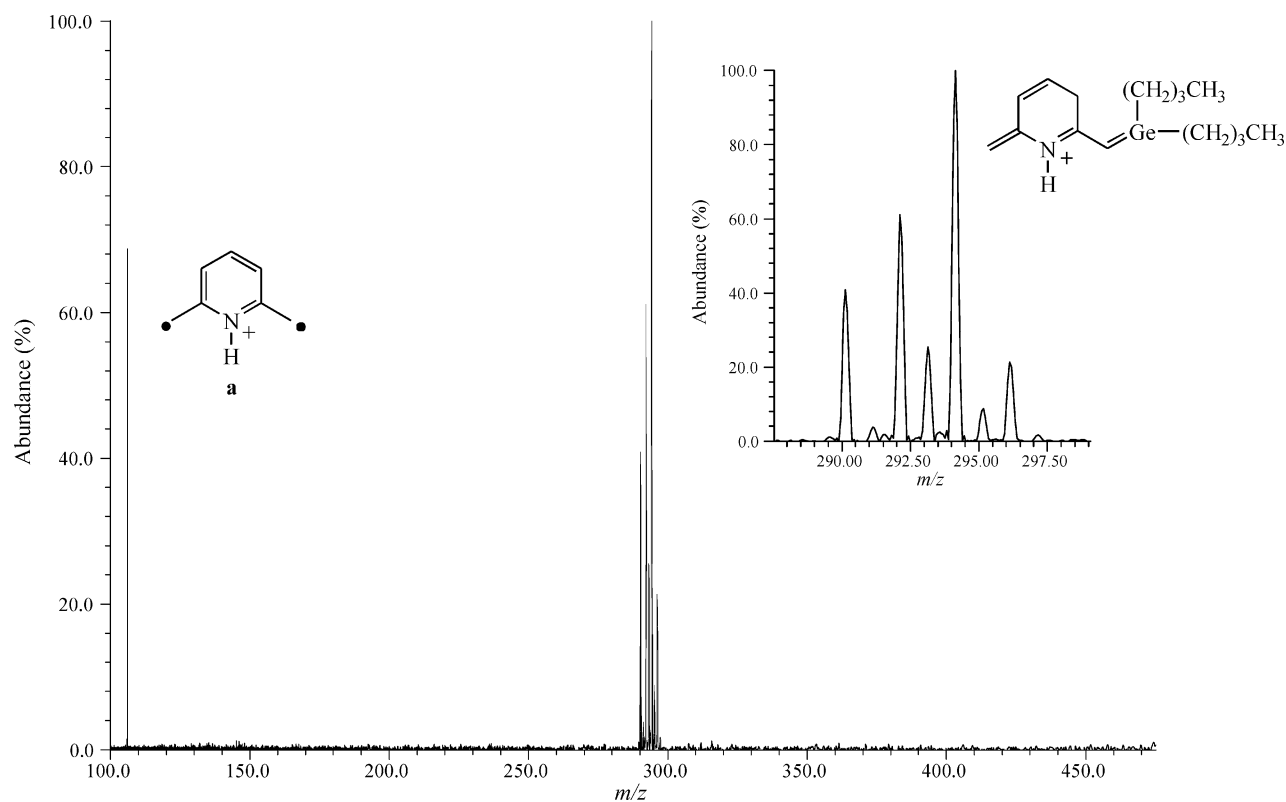
Biradical	Di- <i>tert</i> -butyl nitroxide	<i>tert</i> -Butyl isocyanide	Tributylgermanium hydride	Benzeneselenol
 <b>a</b>	(100%) Addition – C <sub>4</sub> H <sub>8</sub> 2 x (Addition – C <sub>4</sub> H <sub>8</sub> ) <sup>a</sup> Eff. = 46%	(90%) HCN Abstraction (10%) Addition Eff. = 27%	(100%) Addition – C <sub>4</sub> H <sub>10</sub> Eff. = 80%	(70%) Addition (24%) H-abstraction (6%) Adduct – Se 2 x H-abstraction <sup>a</sup> Eff. = 10%
 <b>b</b>	(91%) Addition (9%) Addition – C <sub>4</sub> H <sub>8</sub> 2 x (Addition – C <sub>4</sub> H <sub>8</sub> ) <sup>a</sup> (2 x Addition) – C <sub>4</sub> H <sub>8</sub> <sup>a</sup> 2 x Addition <sup>b</sup> Eff. = 55%	No Reaction	(37%) Addition (63%) H-abstraction 2 x H-abstraction <sup>a</sup> Eff. = 11%	(60%) Addition (40%) H-abstraction 2 x H-abstraction <sup>a</sup> Eff. = 0.9%
 <b>c</b>	(80%) Addition (20%) Addition – C <sub>4</sub> H <sub>8</sub> (2 x Addition) – C <sub>4</sub> H <sub>8</sub> <sup>a</sup> 2 x Addition <sup>b</sup> Eff. = 55%	No Reaction	(76%) Addition (24%) H-abstraction 2 x H-abstraction <sup>a</sup> Eff. = 10%	(81%) Addition (19%) H-abstraction 2 x H-abstraction <sup>a</sup> Eff. = 1%
 <b>d</b>	(100%) Addition 2 x Addition <sup>a</sup> Eff. = 53%	No Reaction	(70%) Addition (30%) H-abstraction 2 x H-abstraction <sup>a</sup> Eff. = 0.6%	(75%) Addition (25%) H-abstraction 2 x H-abstraction <sup>a</sup> Eff. = 0.3%

<sup>a</sup> Secondary products.**Table 2.** Reactions Observed for the Monoradicals **e–g** (Relative Product Abundances Given in Parentheses) and Their Efficiencies (Eff. =  $k_{\text{exp}}/k_{\text{coll}}$ )

Monoradical	Di- <i>tert</i> -butyl nitroxide	<i>tert</i> -Butyl isocyanide	Tributylgermanium hydride	Benzeneselenol
 <b>e</b>	(4%) Addition (96%) Addition – C <sub>4</sub> H <sub>8</sub> Eff. = 80%	(55%) Addition (45%) H-abstraction Eff. = 0.04%	(100%) H-abstraction Eff. = 48%	(100%) H-abstraction Eff. = 4%
 <b>f</b>	(78%) Addition (22%) Addition – C <sub>4</sub> H <sub>8</sub> Eff. = 55%	No Reaction	(100%) H-abstraction Eff. = 10%	(100%) H-abstraction Eff. = 1%
 <b>g</b>	(100%) Addition Eff. = 51%	No Reaction	(100%) H-abstraction Eff. = 0.5%	(100%) H-abstraction Eff. = 0.3%

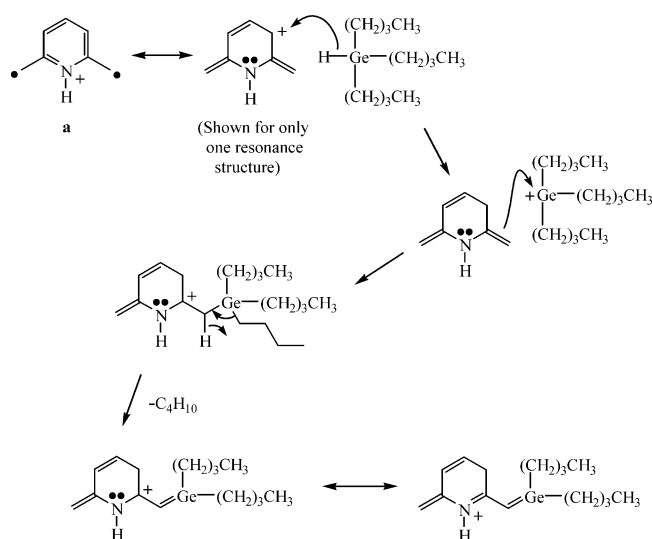
When the singlet biradical **a** was allowed to react with benzeneselenol, similar products (70% due to addition, 24% due to H-atom abstraction) were observed as those formed from the biradicals **b**, **c**, and **d** (Figures 1 and 2), with the exception of one additional product (6% due to addition followed by Se loss). However, **a** was found to react nearly 10 times faster with benzeneselenol (efficiency = 10%) than biradicals **b** and **c**

(efficiency = 0.9% and 1.2%, respectively), approximately 30 times faster than **d** (efficiency = 0.3%), and 2.5–30 times faster than the monoradicals **e–g**. Therefore, we propose that **a** reacts through an ionic pathway rather than a radical pathway with this reagent. The proposed ionic mechanism is shown in Scheme 8. The reaction produces a monoradical that abstracts a hydrogen atom from another benzeneselenol molecule via a radical



**Figure 5.** Reaction of **a** with tributylgermanium hydride for 4 s (nominal pressure  $6.0 \times 10^{-3}$  Torr). Only one possible isomer of the product ion population formed by addition ( $C_4H_{10}$ ) is shown.

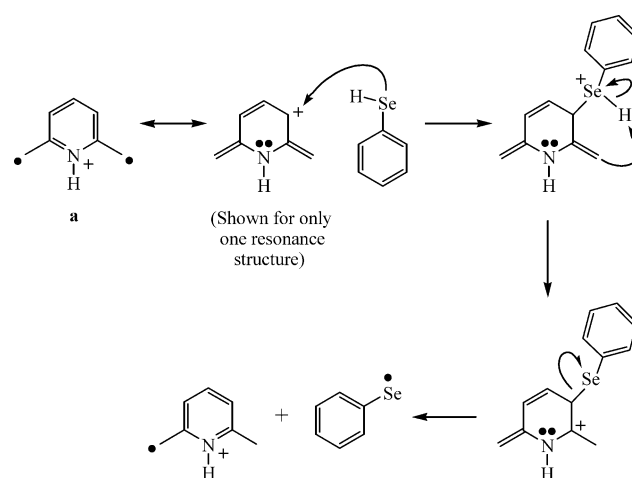
#### Scheme 7



pathway, similarly to the analogous monoradical **e**. Biradicals **b**, **c**, and **d** are concluded to react like their monoradical analogues, while the singlet biradical **a** displays its own distinct reactivity.

In an attempt to explain the observed reactivity ordering for the biradicals and monoradicals ( $b \approx c \approx f > d \approx g$ ), the reaction exothermicities were explored computationally (BPW91/6-311+G(d,p) + ZPVE) by determining the heats of reaction for hydrogen-atom abstraction from tributylgermanium hydride and benzeneselenol by the radicals and biradicals. The enthalpy change for abstraction of a H-atom ranges between  $-6.0$  and  $-7.3$  kcal/mol for tributylgermanium hydride and between  $-16.6$  and  $-17.8$  kcal/mol for benzeneselenol (Table 3). Note

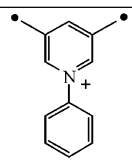
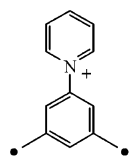
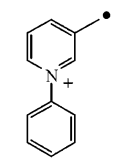
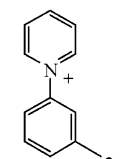
#### Scheme 8



that biradical **b** was not included in this calculation, since the first hydrogen abstraction by this biradical is well approximated by that of biradical **c**. Comparison of the measured reaction rates and the predicted exothermicities for **c**, **d**, **f**, and **g** demonstrates that changes in the enthalpic driving force do not explain the measured trend in the reaction efficiencies. As an example, abstraction of a H-atom from tributylgermanium hydride is calculated to be exothermic by  $-7.3$  kcal/mol for **f** and by  $-6.1$  kcal/mol for **g**; a small difference of 1.2 kcal/mol. However, the charged radical **f** abstracts a hydrogen atom from tributylgermanium hydride 20 times more efficiently (10%) than the charged radical **g** (0.5%). Further, **c** abstracts a hydrogen atom from tributylgermanium hydride with an efficiency 10 times greater than that for benzeneselenol, even though calculations predict the former reaction to be less exothermic by

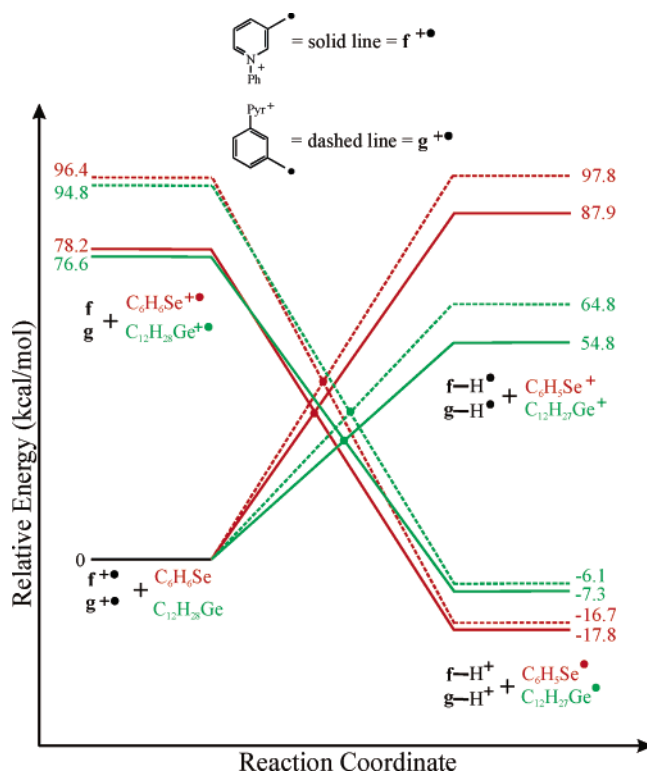


**Table 3.** Calculated (BPW91/6-311+G(d,p) + ZPVE at 298 K) Heats of Reaction (kcal/mol) for Hydrogen-Atom Abstraction from Tributylgermanium Hydride and Benzeneselenol by **c**, **d**, **f**, and **g**

Ion	Tributylgermanium hydride	Benzeneselenol
	-7.2	-17.8
<b>c</b>		
	-6.0	-16.6
<b>d</b>		
	-7.3	-17.8
<b>f</b>		
	-6.1	-16.7
<b>g</b>		

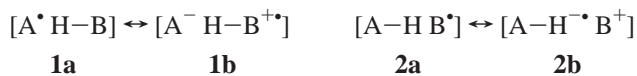
approximately 10 kcal/mol. These examples suggest that the changes in reaction enthalpy do not correlate with the differing reaction efficiencies, and other factors must be taken into account to explain these results.

Previously, we have shown<sup>42,57,58,67,69</sup> that polar effects<sup>70–75</sup> play a crucial role in controlling the reaction efficiencies of charged  $\sigma$ -radicals and  $\sigma,\sigma$ -biradicals. Specifically, the energy of the transition state for a radical reaction is significantly influenced by low-lying charge-transfer resonance structures, which contribute to the electronic structure of the transition state. Anderson and co-workers<sup>76,77</sup> have successfully demonstrated that the height of the reaction barrier for atom transfer between neutral radicals correlates with the energy of an avoided crossing of the ground state and a low-lying (hypothetical) ionic excited state of the reactants and products. The lower in energy the



**Figure 6.** Anderson-type curve-crossing diagram estimated for the reactions of charged radicals **f** (solid line) and **g** (dashed line) with tributylgermanium hydride (green trace) and benzeneselenol (red trace).

excited state lies, the more polar the transition state and the faster the reaction. The relevant ionic excited states for reactions of electrophilic radicals are shown in an equation below (note that the radicals studied here are highly electrophilic<sup>58</sup> due to the electron-withdrawing pyridinium group).



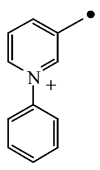
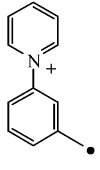
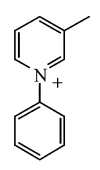
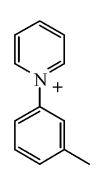
The energy of the reactant-like ionic state (**1b**) decreases as the electron affinity (EA) of the radical  $A^{\bullet}$  increases and the ionization energy (IE) of the substrate  $H-B$  decreases. Similarly, the energy of the product-like ionic state (**2b**) decreases with an increase in EA of  $A-H$  and a decrease in IE of  $B^{\bullet}$ .

To examine the influence of ionic states on the transition-state energy, the vertical electron affinities of **f**, **g**, **f** +  $H$ , and **g** +  $H$  and the vertical ionization energies of benzeneselenol, tributylgermanium hydride, phenylseleno radical, and tributylgermanyl radical were calculated at the BPW91/6-311+G(d,p) level of theory (Tables 4 and 5). Vertical values were used because they are in better agreement with the models developed to understand polar effects in radical reactions.<sup>13,76</sup>

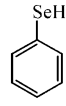
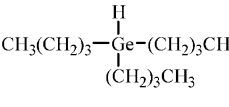
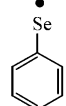
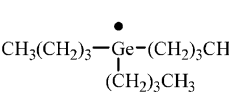
The Anderson-type curve-crossing diagram for the reactions of **f** and **g** with tributylgermanium hydride and benzeneselenol is shown in Figure 6. The ground states for the reactant and product geometries are placed at relative energies corresponding to the calculated thermochemistry of each reaction shown in Table 3. The energy of the ionic states relative to the ground states are approximated by subtracting the EA of the charged species from the IE of the neutral species for both the reactants and products (Tables 4 and 5). (This is a very rough approximation. Actually, the ionization energy of the breaking bond and

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**Table 4.** Calculated (BPW91/6-311+G(d,p) + ZPVE) Vertical Electron Affinities (in eV) for Charged Species **f**, **g**, **f** + H, and **g** + H

Ion	Vertical electron affinity (eV)
	5.63
<b>f</b>	
	4.84
<b>g</b>	
	4.51
<b>f</b> + H	
	4.08
<b>g</b> + H	

**Table 5.** Calculated (BPW91/6-311+G(d,p) + ZPVE) Vertical Ionization Energies (in eV) for Tributylgermanium Hydride and Benzeneselenol, as Well as Phenylseleno and Tributylgermanyl Radicals

Substrate	Vertical ionization energy (eV)
	9.02
	8.95
	8.32
	6.89

the EA of the new bond should be used). Figure 6 shows that the ionic states lie lower in energy for **f** than for **g** because radical **f** is more electrophilic (has a larger EA) than **g**. Hence, it is expected that the ionic states of **f** have a greater stabilizing

influence on the transition state than those of **g**. In fact, the observed reactivity trend **f** > **g** matches this prediction.

Further, the curve-crossing diagram predicts that for both **f** and **g**, the barrier for H-atom abstraction is lower for tributylgermanium hydride than for benzeneselenol, despite the fact that the latter reaction is more exothermic. The faster reaction of tributylgermanium hydride compared to benzeneselenol is the result of a significantly lower product-like ionic state, which has a large contribution to stabilizing the transition state. Specifically, the product-like ionic states lie lower in energy for tributylgermanium hydride (54.8 and 64.8 kcal/mol for **f** and **g**, respectively) than for benzeneselenol (87.9 and 97.8 kcal/mol for **f** and **g**, respectively) because of the low ionization energy of the tributylgermanyl radical (IE = 6.89 eV, Table 5) relative to the phenylseleno radical (IE = 8.32 eV, Table 5). Since monoradicals **f** and **g** show the same reactivity trends as biradicals **b**, **c**, and **d**, respectively, it is inferred that these biradicals are likely influenced by polar effects in a similar manner.

**Reactions with di-tert-Butyl Nitroxide.** Examination of the reactions of the biradicals with the stable free-radical di-tert-butyl nitroxide produced interesting results. Although the four biradicals **a–d** react with this neutral reagent at similar efficiencies (approximately 50%), their primary product distributions vary greatly. For example, biradical **a** reacts exclusively by addition followed by loss of C<sub>4</sub>H<sub>8</sub> (isobutene). The dissociative loss of isobutene is less favorable for the other biradicals (20% and 0% for **c** and **d**, respectively). Interestingly, the reaction of biradical **b** with di-tert-butyl nitroxide reveals a dissociation product in an abundance (9%) that is the average of biradicals **c** and **d**. This finding suggests that **b** reacts equally readily at either radical site. The reaction of the monoradicals **e** and **f** with di-tert-butyl nitroxide yields similar product distributions as the analogous biradicals, **a** and **c**, respectively. Further, reaction of monoradical **g** yields the analogous primary product ion that is obtained for biradical **d**.

Consistent with their high spin ground states, biradicals **b**, **c**, and **d** display monoradical-like reactivity toward di-tert-butyl nitroxide. These species, just like the analogous monoradicals **f** and **g**, undergo rapid radical–radical recombination with the free-radical reagent at similar efficiencies (~50%). Although singlet **a** demonstrated ionic reactivity toward *tert*-butyl isocyanide and the H-atom donors, it is possible that the reaction with di-tert-butyl nitroxide follows a similar radical pathway as for the other biradicals. The reaction with this free radical reagent is the only case in this study in which **a** reacts at a slower rate with a reagent than the analogous monoradical **e** or the other biradicals. In fact, biradical **a** reacts with the free radical approximately 2 times slower (46%) than **e** (85%). This rate decrease in a radical reaction of a singlet biradical can be attributed to an increase in the reaction barrier due to the need to partially uncouple the electrons in the transition state.<sup>34</sup>

## Conclusions

West et al.<sup>39</sup> have predicted that substituting a positively charged group into a position that contains a large coefficient in only one of the NBMOs of *m*-xylylene causes a substantial reduction in the singlet–triplet splitting and results in the generation of a singlet *m*-xylylene derivative. Our results on the reactivity of the 2,6-dimethylenepyridinium ion (**a**) clearly

show that the presence of the charged group has reversed the electronic ground state of biradical **a** from a triplet to a singlet. This is evident in the comparison of the gas-phase reactivity of the charged biradical **a** to that of **b**, **c**, and **d**, all expected to be ground-state triplets, and the analogous monoradicals **e**, **f**, and **g** toward tributylgermanium hydride, *tert*-butyl isocyanide, and benzeneselenol. Biradical **a** reacts drastically faster and through different pathways with these reagents than the other biradicals and monoradicals studied. Most of the reactions of biradical **a** likely follow ionic mechanisms. However, **a** may undergo radical reactions with di-*tert*-butyl nitroxide, albeit slower than the analogous monoradical **e**. The reduced reaction rate for this radical-type reaction is rationalized by the singlet coupling of the biradical electrons in **a**, which results both in a greater barrier and a smaller thermodynamic driving force for radical reactions. Biradicals **b**, **c**, and **d**, calculated to have triplet ground states,

demonstrate radical reactivity analogous to that observed for the monoradicals **f** and **g**. In fact, the rates of reaction of these biradicals are well approximated by the reaction rates of the monoradical analogues.

The observed reactivity trends for hydrogen-atom abstraction from tributylgermanium hydride and benzeneselenol were found not to reflect the calculated reaction enthalpies. Instead, polar effects, as rationalized using the ionic curve-crossing model developed by Anderson and co-workers,<sup>76,77</sup> appear to be a factor in controlling the reactivity of  $\pi,\pi$ -biradicals with triplet ground-states and analogous radicals.

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