Charged Phenyl Radicals

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Abstract: The chemical properties of phenyl radicals with different chemically inert charged substituents in the *ortho*, *meta*, and *para* positions were examined in the gas phase in a Fourier-transform ion cyclotron resonance mass spectrometer. The radicals were generated by replacing a chlorine, bromine, or iodine atom in a radical cation of dihalobenzene with a nucleophile and by cleaving the remaining iodine or bromine atom by collision-activated dissociation. The radicals' structures were characterized by ion−molecule and dissociation reactions and by comparison to the reactivity of isomeric reference ions. *Ab initio* molecular orbital calculations (ROMP2/6-31G*//ROHF/6-31G* + ZPE) carried out for the 2-, 3-, and 4-dehydrophenylsulfonium ions suggest that these three species are nearly equal in energy and significantly less stable than the isomeric thiophenol radical cation. Most of the charge density is localized on the substituent in the charged phenyl radicals examined computationally. The odd-spin density at the radical site is calculated to be the same as in the neutral phenyl radical. These computational results predict chemical properties drastically different from those typical for conventional organic radical cations, *e.g.*, the radical cation of thiophenol. This was found to be the case. Phenyl radicals with different charged groups in the *meta* or *para* position yield the same reaction products as the neutral phenyl radical (the *ortho* isomers rearrange upon collisions). Further, charged and neutral phenyl radicals show similar reactivity trends toward different substrates. Examination of the reactivity of radicals of various sizes and with the charged group in different locations with respect to the radical site suggests that the reaction efficiency toward a given substrate is predominantly determined by the electron deficiency at the reacting radical site. All these findings parallel those reported earlier for neutral phenyl radicals, and suggest that phenyl radicals with a chemically inert charged substituent in a remote position provide a useful model for the examination of the properties of neutral phenyl radicals in the gas phase.

Introduction

Distonic radical cations[1] (ionized biradicals, zwitterions, and ylides) commonly possess two potentially reactive, spatially separated sites, a charge site and a radical site. In principle, these species can undergo ionic as well as radical reactions.[2] Both types of reactivity have been reported.[2−14] Distonic ions with a chemically inert charge site are expected to predominantly undergo radical reactions and thereby provide a means to study gas-phase radical chemistry by using mass spectrometry.[7−9] This possibility is attractive because mass spectrometry experiments would allow the purification and manipulation of gaseous free radicals carrying a charged substituent.

For a distonic radical cation to provide a useful model of a reactive neutral radical, the ion must have a coordinatively saturated and chemically inert charge site separated from the radical site by a rigid spacer.[5,10,13,14] This arrangement prevents a neutral reagent from reacting or binding at the charge site. We recently published a short preliminary report[9] on the use of Fourier-transform ion cyclotron resonance mass spectrometry (FT/ICR) to generate distonic radical cations wherein the charge and radical sites are held apart by a phenyl ring. We describe here in detail the synthesis and experimental and computational characterization of a number of gaseous phenyl radicals with different chemically inert charged substituents. The reactivity of these radicals toward various substrates is reported and the effects of the size of the radical, the type of the charged group, and the distance between the charge and radical sites are evaluated.

Experimental Section

All experiments were performed using an Extrel Model 2001 Fourier transform ion cyclotron resonance mass spectrometer (FT/ICR). This instrument contains a differentially pumped dual cell which is placed within the magnetic field produced by a 3.0-T superconducting magnet operated at 2.3−2.8 T. The nominal base pressure is less than 10^{-9} Torr, as maintained by two Balzers turbomolecular pumps (330 L s^{-1}), each backed with an Alcatel mechanical pump. The pressure is measured with two ionization gauges located on either side of the dual cell. The two cells are separated by a common wall (the conductance limit) which contains a 2 mm hole in the center. Ions were transferred from one cell into the other by grounding the conductance limit plate for approximately 150 μs. Unless otherwise noted, this plate and the other two trapping plates were maintained at +2 V.

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The halogenated benzenes (diiodo, bromoiodo, and chloroiodo) were introduced at a nominal pressure of (1.0−1.5) × 10^{-7} Torr into one side of the dual cell by using a heated solids probe or a variable leak valve. The appropriate nucleophile was added at a nominal pressure of about 2 × 10^{-7} Torr into the same cell through a batch inlet system or by using the solids probe. The mixture was subjected to electron ionization (typically 20 eV electron energy, 8 μA emission current, 50 ms ionization time) which resulted in an abundant signal for the halobenzene radical cation. These radical cations were allowed to react with the nucleophile to produce a halogen displacement product (the reaction times used ranged from 750 ms up to 10 s).

The ions formed upon the halogen displacement reaction were transferred into the other side of the dual cell and cooled for 1 s by collisions with the neutral molecules present in this cell (the reagent to be used in the final stage of the experiment). The ions were then isolated by ejecting all unwanted ions from the cell through the application of a stored-waveform inverse Fourier transform (SWIFT)[15] excitation pulse to the excitation plates of the cell (Extrel SWIFT module). After isolation, argon was pulsed into the cell via a pulsed valve assembly (peak nominal pressure was 6 × 10^{-6} to 1 × 10^{-5} Torr in the cell), and the remaining carbon−iodine bond was cleaved by collisionally activating the ions for about 1 s by employing the sustained off-resonance (SORI)[16] technique at a frequency 0.5−1.0 kHz higher than the cyclotron frequency of the ions. The product ions were cooled for about 0.5 s through collisions with the neutral molecules present in the cell.

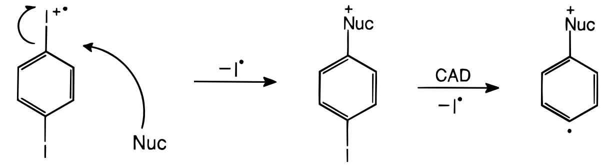
The charged phenyl radicals were isolated by ejecting all other ions from the cell as described above. The isolated ions were allowed to undergo reactions with a neutral reagent for a variable period of time (typically 1−20 s). After reaction, the ions were excited for detection by using "chirp" excitation or the SWIFT excitation method (0.5 cm final radius for all ions). All the measured spectra are the average of 50 transients and were recorded as 64 k data points and subjected to one zero fill *prior to* Fourier transformation.

Since the reactions studied under the conditions described above follow pseudo-first-order kinetics, the second-order rate constant (k_{exp}) for each ion−molecule reaction was obtained from a semilogarithmic plot of the relative abundance of the reactant ion *versus* time. The collision rate constants (k_{coll}) were calculated using the parametrized trajectory theory.[17] The reaction efficiencies are given by $k_{\text{exp}}/k_{\text{coll}}$. The accuracy of the rate constant measurements is estimated to be ±50%, while the precision is usually better than ±10%. The pressure readings were corrected for the sensitivity of the ion gauge toward each neutral reagent[18] and for the pressure gradient between the dual cell and the ion gauge. The latter correction factor was obtained by measuring the rates of reactions with known rate constants involving the neutral molecules of interest.

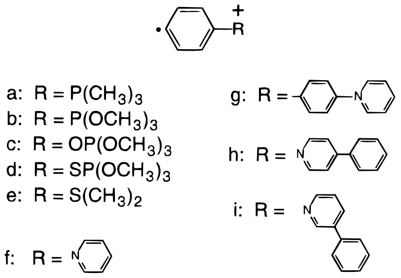
On-resonance collision-activated dissociation[19] (CAD) was used to examine the structures of some of the product ions. The ions were generated by the SORI technique as described above except that a static argon pressure of 1 × 10^{-7} Torr was used. The use of a lower pressure resulted in a smaller number of activating collisions during CAD, which is desirable for ion structure determination.[20] The fragment ions were detected in the usual manner.

Ab initio molecular orbital calculations were carried out using the Gaussian 92 Revision F suite of programs.[21] The geometries were fully optimized at the ROHF/6-31G* level of theory (the ROHF/3-21G* level was used for a few calculations as specified in the text). Zero-point vibrational energies (ZPE) were calculated from the ROHF/6-31G* (or ROHF/3-21G* if so specified) harmonic frequencies and scaled by a factor of 0.9 to account for the systematic overestimation of the vibrational frequencies by the Hartree−Fock method.[22] Single-point energies were calculated for selected structures at the ROMP2/6-31G*//ROHF/6-31G* + ZPE level of theory. The force constant matrices obtained for the stationary points were confirmed to have the correct number of negative eigenvalues (zero for equilibrium structures).

Scheme 1



Scheme 2



Results and Discussion

Synthesis. A multistep procedure (Scheme 1) was used to generate various charged phenyl radicals in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer (FT/ICR). The first step of the synthesis involves the generation of a haloiodobenzene radical cation (diiodo, bromoiodo, or chloroiodo; for an example, see Figure 1a). *Ipso* substitution[23] of an iodine, chlorine, or bromine atom with a neutral nucleophile yields the desired substituted iodobenzene ion (Figure 1c). Different nucleophiles that do not carry heteroatom bonded hydrogen atoms, *i.e.*, whose ionic forms are not strong Brönsted acids, were used in this study (see Scheme 2 for examples). These species were expected (and found) to yield phenyl radicals with chemically inert charge sites when the iodine atom was cleaved by sustained off-resonance induced collision-activated dissociation[16] in the other side of the dual cell (Figures 1e and 1f).[9]

Structural Characterization. The structures of the charged phenyl radicals were examined by allowing them to react with neutral reagents that have proven useful in the structural characterization of other organic radical cations, *e.g.*, dimethyl disulfide[6] and triethylamine.[24] All the radicals studied react with dimethyl disulfide by exclusive $^{\bullet}SCH_3$ abstraction that provides strong support for a distonic structure for the reactant ions.[6] Plots of the natural logarithm of the relative abundance

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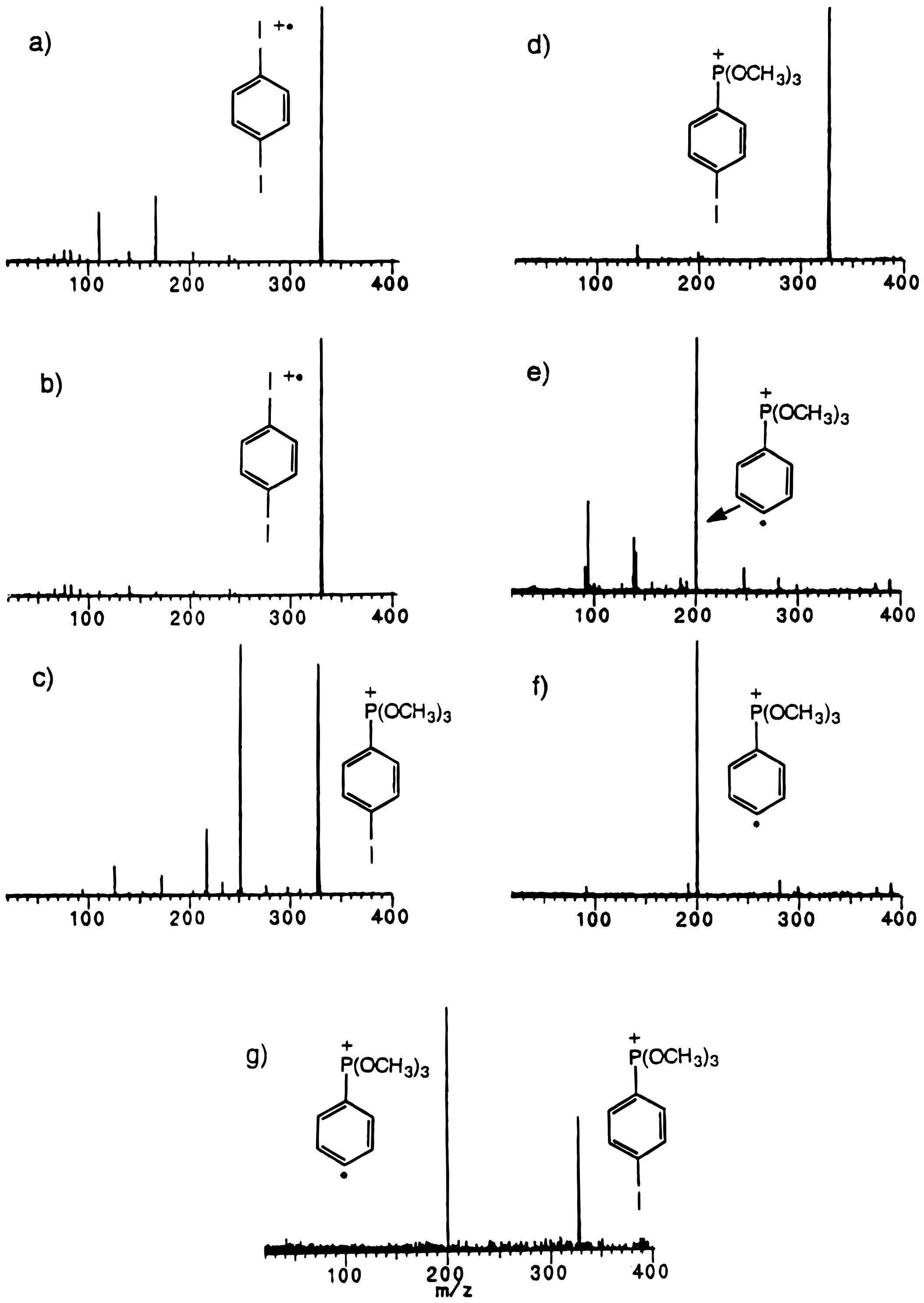


Figure 1. An example of the method used to generate charged phenyl radicals. (a) Electron ionization of 1,4-diiodobenzene (*m/z* 330) was followed by (b) isolation of the radical cation of 1,4-diiodobenzene (*m/z* 330) in one side of the dual cell (this step was skipped in most experiments). (c) Reaction of the radical cation of 1,4-diiodobenzene with trimethyl phosphite yielded the 4-iodophenyltrimethoxyphosphonium cation (*m/z* 327) which was (d) transferred into the other side of the dual cell and isolated. (e) Collision-activated dissociation (SORI) of the ion of *m/z* 327 produced the 4-dehydrophenyltrimethoxyphosphonium cation (**b**; *m/z* 200) (f) that was isolated. (g) The reaction of the charged phenyl radical with allyl iodide occurs by iodine atom abstraction (shown for 2 s reaction time at a nominal pressure of 1.2 × 10^{-7} Torr).

of the reactant ions vs. time demonstrate that the reactions follow *pseudo*-first order kinetics (for example, see Figures 2a and 2b; the *ortho* isomers are an exception: Figure 2c). The reactions were found to proceed to completion (again, with the exception of the *ortho* isomers). These findings suggest that the entire reactant ion population has the same distonic structure.

The structure of **e** (R = $S(CH_3)_2$; Scheme 2) was examined earlier[9] by collision-activated dissociation experiments. This radical was found to dissociate by predominant loss of $^\bullet CH_3$ (minor loss of $^\bullet SCH_3$ was also observed; Scheme 3). This dissociation behavior is analogous to that observed for protonated dimethyl sulfoxide (loss of $^\bullet CH_3$ dominates; Scheme 3), suggesting a sulfonium charge site for **e**. In order to provide further support for this structural assignment, the reactivity of **e** was compared to that of two isomeric reference ions, the radical cations of benzyl methyl sulfide and *p*-methylthioanisole. The radical cation of benzyl methyl sulfide readily abstracts an electron from dimethyl disulfide while the radical cation of

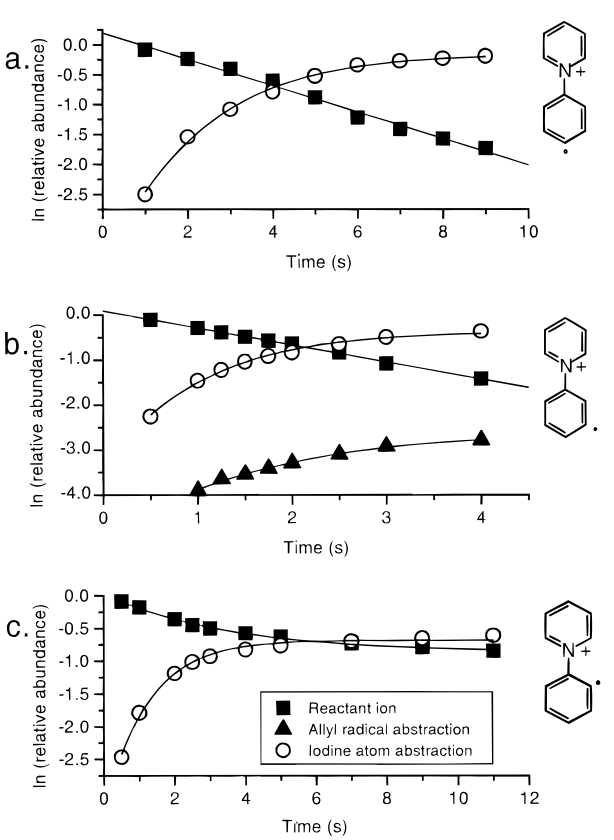
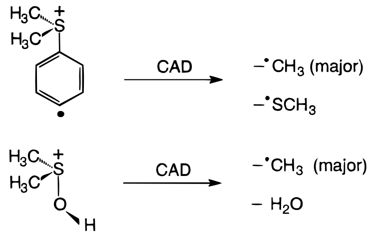


Figure 2. Temporal variation of ions during reaction of allyl iodide with (a) the charged phenyl radical **f** (the nominal pressure of allyl iodide was 1.0 × 10^{-7} Torr), (b) its *meta* isomer (the nominal pressure of allyl iodide was 2.4 × 10^{-7} Torr), and (c) its *ortho* isomer (the nominal pressure of allyl iodide was 2.4 × 10^{-7} Torr). The data points measured for the products and the reactant in (c) are connected by arbitrary smooth lines.

Scheme 3



p-methylthioanisole[9] is unreactive.[25a] These findings clearly distinguish the charged phenyl radical **e** from the reference ions.

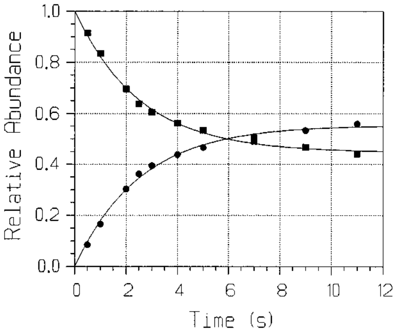
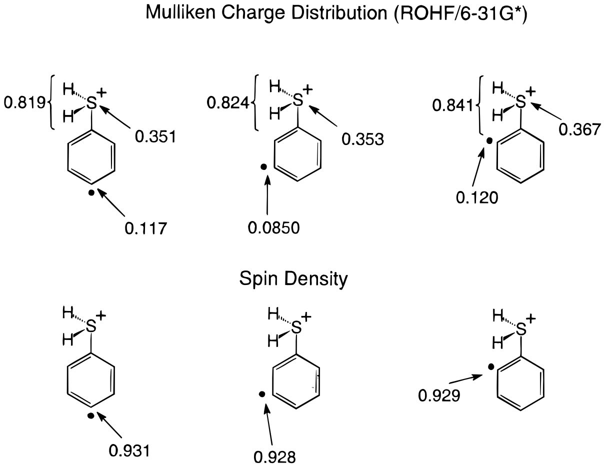


Figure 3. The relative abundances of the reactant and product ions are shown as a function of time for the reaction of the *ortho* isomer of **f** with allyl iodide (nominal pressure 2.4 × 10^{-7} Torr). The lines drawn through the data points represent the best fit to the rate equation corresponding to two parallel reaction pathways, abstraction of an iodine atom from allyl iodide by **f** in competition with isomerization of **f** to an unreactive ion upon collisions with allyl iodide.

Scheme 4



Different distonic isomers of some of the charged phenyl radicals were also examined. The charged phenyl radical **c** with the trimethylphosphonium charge site (R = $OP(OCH_3)_3$) in the *para* position (Scheme 2) was shown to be distinct from its *meta* isomer based on different reaction efficiencies (*e.g.*, the efficiency for the reaction with allyl iodide is 0.24 for the *meta* isomer and 0.12 for the *para* isomer). The same applies to the *meta* and *para* forms of the radical with the dimethylsulfonium charge site (R = $S(CH_3)_2$). However, the radical thought to be the *ortho* isomer was found to be unreactive toward dimethyl disulfide and to readily abstract an electron from triethylamine (efficiency about 0.6). Both these findings suggest that the *ortho* radical has rearranged to a conventional radical cation, likely that of *o*-methylthioanisole.[25b]

The charged phenyl radical **f** is distinguished from its *meta* isomer based on different products formed upon reaction with allyl iodide. Complete and exclusive iodine atom abstraction was observed for **f** (Figure 2a) while its *meta* isomer shows both iodine and allyl abstraction (Figure 2b). The reactions of these two ions follow *pseudo*-first-order kinetics, which differentiates them from their *ortho* isomer (Figure 2c). Time-resolved reaction data measured for the *ortho* isomer were fit to various rate equations. The best fit (Figure 3) was obtained for the rate equation corresponding to two parallel reaction pathways, abstraction of an iodine atom in competition with isomerization of the reactant ion to an unknown unreactive form upon collisions with allyl iodide. Based on this fit, approximately 50% of the *ortho* isomer undergoes isomerization within the collision complex (Figure 3).

Ab Initio Molecular Orbital Calculations. *Ab initio* molecular orbital calculations were used to examine the relative stabilities and the charge and odd-spin distributions of isomeric charged phenyl radicals by using the radical cation of thiophenol and its three distonic isomers as the model system (Schemes 4 and 5). At the ROMP2/6-31G*//ROHF/6-31G* + ZPE level of theory, the three distonic ions were found to be nearly

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(25) (a) Conventional radical cations with ionization energies (IE) <8.1 eV are usually (ref 6) unreactive toward dimethyl disulfide (IE = 7.5 eV for *p*-methylthioanisole, ref 26a; IE = 8.1 eV for dimethyl disulfide, refs 26b,c). (b) The *o*-methylthioanisole radical cation was not examined but can be expected to show the same behavior as the radical cation of *p*-methylthioanisole. Both radical cations are expected to be unreactive toward dimethyl disulfide (see ref 25a). However, triethylamine has a low enough ionization energy (IE = 7.5 eV; ref 26a) to be readily oxidized by both radical cations.

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Scheme 5

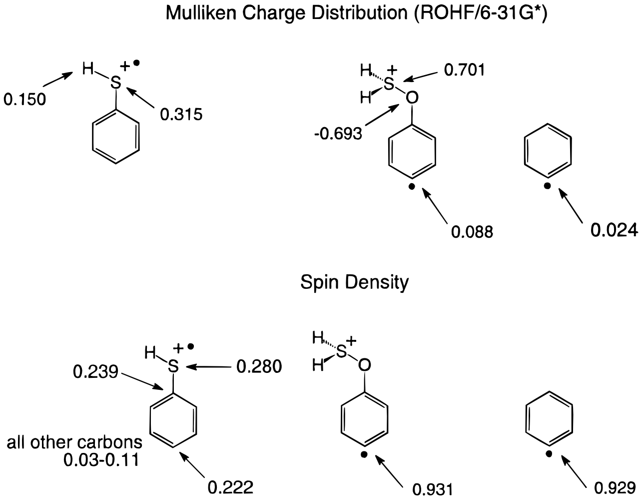

Table 1. Calculated Absolute and Relative Energies of the Conventional Thiophenol Radical Cation and Its Distonic Isomers (Structures Are Shown in Schemes 4, 5 and 6)

ion	absolute energy (hartrees)[a]	relative energy (kcal mol^{-1})
ortho isomer	−628.607116	53.2
meta isomer	−628.606383	53.6
para isomer	−628.606141	53.8
ionized thiophenol	−628.691870	0

[a] Energy at the ROMP2/6-31G*//ROHF/6-31G* + ZPE level of theory.

isoenergetic, and to lie 53−54 kcal mol^{-1} higher in energy than the radical cation of thiophenol (Table 1). The lowest energy conformer of all four ions has C_s symmetry. The *ortho* and *meta* distonic ions with the SH$_2$ hydrogens pointing toward the radical site were calculated to lie about 1 kcal mol^{-1} lower in energy than the conformers with the hydrogen atoms pointing away from the radical site (not shown). The transition state energy for rotation of the SH$_2$ group in the most stable conformer of the *para* isomer was found to be low (4 kcal mol^{-1} at the ROHF/6-31G* level).

The odd spin density in the thiophenol radical cation is delocalized over the entire molecule (Scheme 5). In contrast, the charged phenyl radicals are localized σ-radicals. In each species, one of the ring carbons has an odd spin density of the same magnitude (0.928−0.931 e; Scheme 4) as in the neutral phenyl radical (0.929 e; Scheme 5). Based on this result, the chemical properties of the charged phenyl radicals may be expected to resemble the properties of the neutral phenyl radical more than those of the thiophenol radical cation.

Most of the Mulliken charge in the thiophenol radical cation was found in the S−H group (0.465; Scheme 5). Similarly, much of the charge density is localized on the substituent in the distonic ions (0.819−0.841; Scheme 4). Hence, these species are much more polar than the neutral phenyl radical.[27] Further, the radical site of the charged radicals is calculated to be significantly more electron deficient than that of the neutral phenyl radical (0.085−0.120 vs. 0.024; Schemes 4 and 5). This electron deficiency should enhance the electrophilic character of the radical site and thereby modify the reactivity from that characteristic of the neutral phenyl radical. Comparison of the charge and odd-spin distributions in the *para* distonic isomers of the radical cations of thiophenol and phenoxythiol (Schemes 4 and 5) suggests that the electrophilicity should be somewhat reduced if the charge-bearing sulfur atom is separated from the phenyl ring by a heavy atom.

Scheme 6

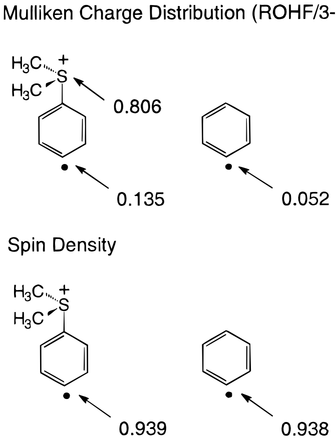

Table 2. Efficiency (k_{exp}/k_{coll}) of $^{\bullet}\mathrm{SCH_3}$ Abstraction from Dimethyl Disulfide and $\mathrm{I^{\bullet}}$ Abstraction from Allyl Iodide by Selected *para*-Substituted Charged Phenyl Radicals

ion[a]	charge site R =	k_{exp}/k_{coll}	
		dimethyl disulfide	allyl iodide
a	$-P^+(CH_3)_3$	$\simeq$0.04[b]	0.13
b	$-P^+(OCH_3)_3$	$\simeq$0.05[b]	$\simeq$0.18[b]
c	$-OP^+(OCH_3)_3$	0.01	0.12
d	$-SP^+(OCH_3)_3$	0.02	0.13
e	$-S^+(CH_3)_2$	0.06	0.19
f	$-N^+C_5H_5$	0.03	0.14

[a] Ions are shown in Scheme 2. [b] Interfering reaction of the ion with the phosphorus nucleophile ($(CH_3)_3P$ or $(CH_3O)_3)P$) diffusing from the other side of the dual cell makes the value less accurate.

In addition to the simple model compounds discussed above, calculations were carried out for one of the charged phenyl radicals that was examined experimentally (see the following discussion). The ion **e** (R = S(CH$_3$)$_2$) was found to have C_s symmetry (at the ROHF/3-21G* level of theory; Scheme 6), just like the other charged radicals studied. Again, most of the charge was found at the sulfur atom (0.806), while an odd-spin density (0.939 e) comparable to that of the neutral phenyl radical (0.938 e) was calculated for the carbon in the *para* position (Scheme 6). The charge density at the carbon radical site was found to be greater than that of the neutral phenyl radical (0.135 vs. 0.052; Scheme 6). These results parallel those obtained for the three distonic isomers of ionized thiophenol. Similar findings were made for the 4-dehydroanilinium ion (discussed later; also see Scheme 8). At the ROHF/3-21G* level of theory, this species is calculated to carry most of the charge at the ammonium group (0.448) and most of the odd-spin density at the *para* carbon (0.939 e). The radical site carries a Mulliken charge similar to that at the radical site of the other model distonic ions studied (0.128).

Comparison of the Reactivity of Charged Phenyl Radicals and Neutral Radicals. The computational results suggest that the charged phenyl radicals studied are localized σ-radicals with a similar odd spin density as in the neutral phenyl radical, and that the type and location of the charged substituent does not greatly affect the odd spin density. Hence, if the charge site of these radicals is chemically inert, their reactivity is expected to resemble that of the neutral phenyl radical and to be quite different from the reactivity typical for organic radical cations. This was found to be the case.

The products formed upon reactions of phenyl radicals with different types of charged substituents (with the exception of the *ortho* isomers that isomerize readily) were found to be the same as those reported for neutral phenyl radicals. For example, the charged phenyl radicals react with dimethyl disulfide by

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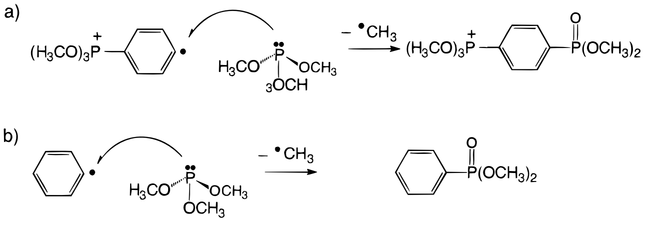
(27) *Free Radicals*; Kochi, J. K., Ed., Wiley: New York, 1973.

Scheme 7



exclusive $^{\bullet}SCH_3$ abstraction (see Table 2 for examples), a reaction that also occurs for the neutral phenyl radical.[28] In sharp contrast, most conventional radical cations either react[2,6] with dimethyl disulfide by electron transfer or are unreactive (for isomers of the charged phenyl radicals studied here, see discussion on structural characterization). Further, neutral alkyl and aryl radicals readily abstract an iodine atom from alkyl iodides, *e.g.*, allyl iodide.[27,30] Similarly, all the charged phenyl radicals studied rapidly abstract an iodine atom from allyl iodide (Table 2; also a trace of allyl radical abstraction was occasionally observed). On the other hand, conventional organic radical cations typically abstract both an allyl group and an iodine atom from allyl iodide.[31]

The above results demonstrate that the types of products obtained upon reactions of the charged phenyl radicals do not depend on the structure of the charged group. Hence, the reactivity toward different substrates was further explored by allowing just a few selected charged phenyl radicals to react with a number of additional substrates whose reactions with neutral alkyl or phenyl radicals have been examined earlier by others.

The neutral phenyl radical has been reported[29] to react with trimethyl phosphite in solution by $CH_3^{\bullet}$ replacement (Scheme 7b). The same reaction was observed for the gaseous charged phenyl radical **b** ($R = P(OCH_3)_3$; Scheme 7a). Interaction of the charged phenyl radical **a** ($R = P(CH_3)_3$) with trimethylphosphine also leads to $CH_3^{\bullet}$ replacement. The reaction of this reagent has not been examined with the neutral phenyl radical.

Neutral radicals are known to readily undergo addition reactions. For example, the phenyl radical reacts with oxygen to form $C_6H_5{-}O{-}O^{\bullet}$ in solution and in the gas phase.[32] Adduct formation was also observed for charged phenyl radicals upon reaction with oxygen (the species studied were **a**, $R = P(CH_3)_3$, **b**, $R = P(OCH_3)_3$, and the *meta* isomer of **e**, $R = S(CH_3)_2$). Further, neutral radicals commonly react with cyclohexene by addition and by hydrogen atom abstraction.[30] Similarly, interaction of charged phenyl radicals with cyclohexene was found to lead to addition and abstraction of a hydrogen atom (the species studied were **b**, $R = P(OCH_3)_3$, and **f**, $R = NC_5H_5$). Reaction of the neutral phenyl radical with allyl bromide occurs via addition to the terminal methylene carbon followed by loss of a bromine atom.[30] Likewise, the charged phenyl radical **a** ($R = P(CH_3)_3$) reacts with allyl bromide by predominant allyl radical abstraction (slower bromine atom abstraction also takes place).

The rate of abstraction of a specific atom or group of atoms from different substrates by a given neutral radical generally increases with the exothermicity of the reaction.[27,33] Hence, it is not suprising that all the charged phenyl radicals studied thus far have been found[34] to abstract a hydrogen atom from benzeneselenol more readily than from thiophenol (the difference in the enthalpy change for these two reactions is determined by the relative homolytic bond dissociation energies of the substrates, $D^{298}(S{-}H) = 83$ kcal/mol for thiophenol[35b] and $D^{298}(Se{-}H) = 78$ kcal/mol for benzeneselenol[35a]). For example, **e** ($R = S(CH_3)_2$) reacts with benzeneselenol at an efficiency of 0.07 and with thiophenol at an efficiency of 0.01.[34] When there is no difference in the thermodynamic driving force for abstraction reactions involving different neutral substrates ($\Delta(\Delta H_{\text{reaction}}) \simeq 0$), a neutral radical is usually more reactive toward the substrate with the lower homolytic bond dissociation energy.[33] The same trend was observed here for the charged phenyl radicals. For example, all the species studied react significantly more efficiently with allyl iodide than with dimethyl disulfide (Table 2) in spite of the fact that the driving force for both reactions[36] is approximately 20 kcal mol^{-1} (*e.g.*, **f**, $R = NC_5H_5$, reacts with allyl iodide and dimethyl disulfide at efficiencies of 0.14 and 0.03, respectively; Table 2). The enhanced reactivity toward allyl iodide is attributed to the fact that the homolytic C–I bond strength in this reagent is less than the S–S bond strength in dimethyl sulfide (41 and 65 kcal mol^{-1}, respectively).[26a]

Effects of the Charged Substituent. The findings discussed above demonstrate that the charged phenyl radicals react with neutral reagents via pathways analogous to those of the neutral phenyl radical. However, the reaction rates (efficiencies) are likely to be influenced by the presence of the charged substituent. Several experiments were carried out in order to investigate the effects of the charged group.

Comparison of the reaction efficiencies measured for phenyl radicals with different charged groups attached to the *para* carbon suggests that their reactivity is not very sensitive to the nature of the charged group (Table 2). For example, the phenyl radicals **a** ($R = P(CH_3)_3$), **b** ($R = P(OCH_3)_3$), **e** ($R = S(CH_3)_2$), and **f** ($R = NC_5H_5$) carry different charged groups and yet react at comparable efficiencies (Table 2: dimethyl disulfide, 0.03–0.06; allyl iodide, 0.13–0.19).

The distance separating the charge and radical sites appears to have some control over the reactivity of the charged phenyl radicals. This is best illustrated by considering the reactivity of species with identical charged groups separated from the radical site by differing distances. The charged phenyl radicals **f** and **g** contain the same pyridinium charge site. However, the radical site of **g** is approximately 3 Å further away from the charge site since these sites are separated by two phenyl rings instead of one. As expected, **g** was found to be less reactive than **f** (**g**: no observable products vs. **f**: 0.03 efficiency toward dimethyl disulfide; **g**: 0.02 vs. **f**: 0.14 efficiency toward allyl iodide; see Figure 4 for reactions with allyl iodide). In order to rule out the possibility that the differing sizes of **f** and **g** cause the observed difference in reactivity, two isomers of **g** were also examined. The species **h** and **i** have the same size as **g** but their charge and radical sites are separated by a similar distance as in **f**. Both **h** and **i** react with allyl iodide at an efficiency comparable to that of **f** (**h**: 0.09, **i**: 0.11 vs. **f**: 0.14; Figure 4). This result suggests that the factor controlling the

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[36] The homolytic S–S bond strength is 65 kcal mol^{-1} in dimethyl disulfide; the newly formed homolytic C–S bond strength is estimated to be 85 kcal mol^{-1} based on neutral thioanisole (ref 26a); the homolytic C–I bond strength is 41 kcal mol^{-1} in allyl iodide; the newly formed homolytic C–I bond strength is estimated to be 65 kcal mol^{-1}, based on neutral iodobenzene (ref 26a).

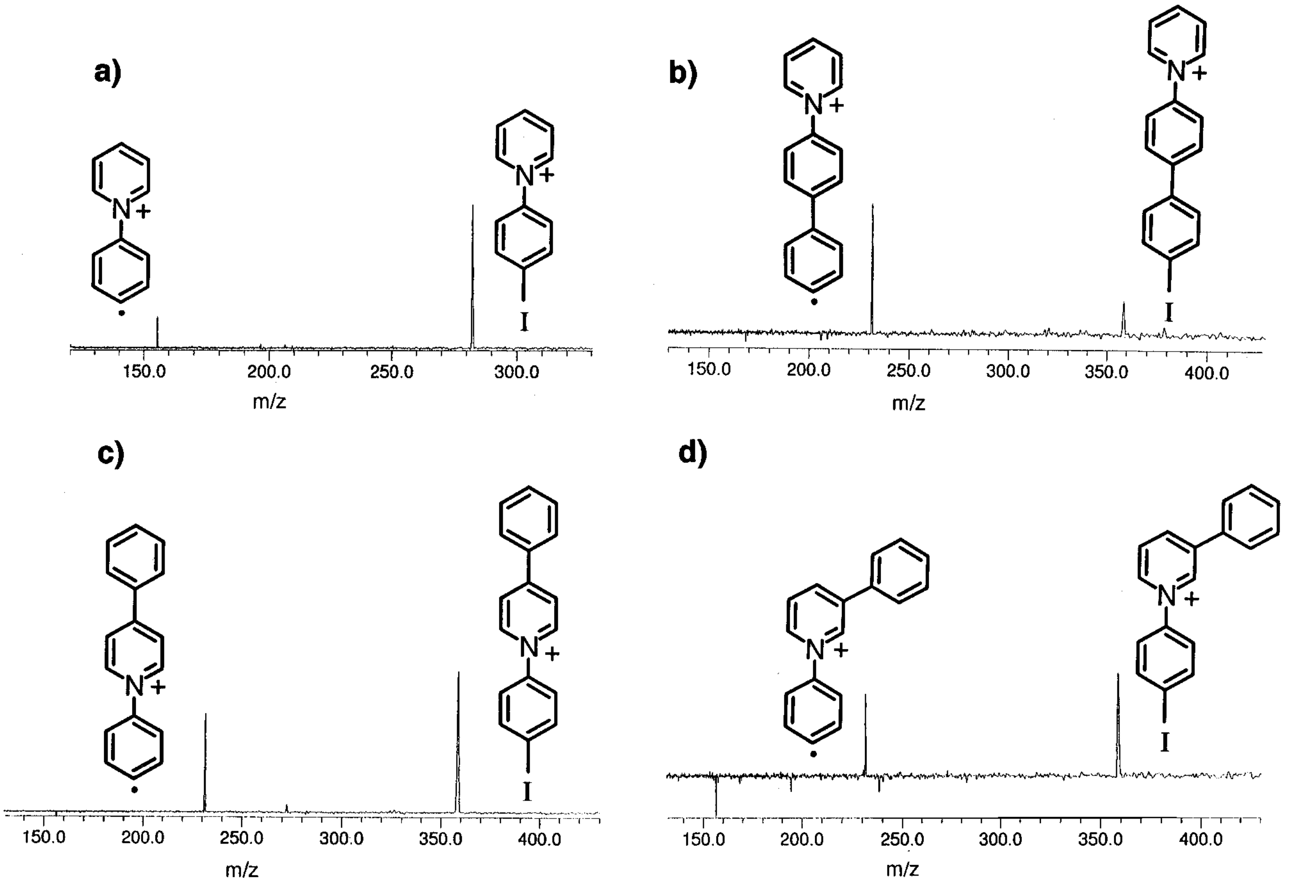

Figure 4. Reaction of allyl iodide (nominal pressure 1.2×10^{-7} Torr) for 9−10 s with several charged phenyl radicals: (a) **f**, (b) **g**, (c) **h**, and (d) **i**.

reactivity of these charged phenyl radicals is the distance between the charge and radical sites rather than the size of the radical.

The findings discussed above are readily rationalized based on the observation that electron-withdrawing substituents generally enhance the reactivity of neutral radicals toward electron-rich substrates. For example, the *p*-nitrophenyl radical abstracts a $^{\bullet}SCH_3$ group from dimethyl disulfide eleven times faster than the unsubstituted phenyl radical.[37] Further, perfluorinated alkyl radicals have been reported to be more reactive than the corresponding unfluorinated radicals toward various substrates (*e.g.*, $CF_3CF_2^{\bullet}$ reacts with tributyltin hydride approximately 100 times faster than $CH_3CH_2^{\bullet}$).[37] Hence, the enhanced reactivity observed for the charged phenyl radicals with the smaller charge/radical site separation may be attributed to a more electron deficient radical site. Indeed, *ab initio* molecular orbital calculations (discussed above) predict a notably greater positive charge at the radical site when the charged sulfonium substituent is directly attached to the phenyl ring (*e.g.*, 0.117 in the *para* distonic isomer of ionized thiophenol, Scheme 4) than when it is separated from the phenyl ring by one oxygen atom (*e.g.*, 0.088; Scheme 5). The increased electron deficiency at the radical site may affect both the reaction exothermicity (unknown for most of the reactions studied here) and the barrier heights. The curve crossing model[38] rationalizes the lowering of barrier heights for reactions of electron deficient radicals as originating from a significant contribution of a charge transfer configuration in the transition state.[38]

Other Considerations. The factors controlling the reactivity of the charged phenyl radicals were further explored by *ab initio* molecular orbital calculations. Chlorine atom transfer from methyl chloride to the neutral phenyl radical and to the 4-dehydroanilinium ion (Scheme 8) and thiomethyl transfer from dimethyl disulfide to the neutral phenyl radical and to the charged phenyl radical **e** ($R = S(CH_3)_2$; Scheme 9) were examined as model reactions. All four reactions were found to be highly exothermic (at the ROHF/3-21G* + ZPE level of theory; Table 3). The enthalpy change calculated for the chlorine atom abstraction by the 4-dehydroanilinium ion ($\Delta H^0_{\text{reaction}} = -10.9$ kcal mol^{-1}; Scheme 8) is slightly smaller (by 3 kcal mol^{-1}) than that calculated for the neutral phenyl radical ($\Delta H^0_{\text{reaction}} = -13.9$ kcal mol^{-1}; this value is in reasonable agreement with $\Delta H^{298}_{\text{reaction}} = -11.3$ kcal mol^{-1}, obtained by using experimental literature values; see Table 3). The thiomethyl abstraction reaction was calculated to be slightly more exothermic (1.7 kcal mol^{-1}) for the charged phenyl radical **e** than for the neutral phenyl radical (Scheme 9). Hence, the charged substituent does not significantly affect the driving force for either reaction. The same has been found[34] to be true for hydrogen atom abstraction reactions.

In the most stable gas-phase collision complex found for the 4-dehydroanilinium ion and methyl chloride, the methyl chloride molecule is hydrogen bonded to the ammonium moiety (Scheme 10a; Table 4). The most stable product complex contains the methyl radical about 3.4 Å apart from the chlorine atom that is attached to the phenyl ring (Scheme 10b). This complex lies 1.6 kcal mol^{-1} lower in energy than the reactant complex (Table 4). Hence, chlorine atom abstraction is an exothermic (although not barrierless) process within this collision complex, in spite of the possibility for a stabilizing hydrogen bond formation at the charge site.

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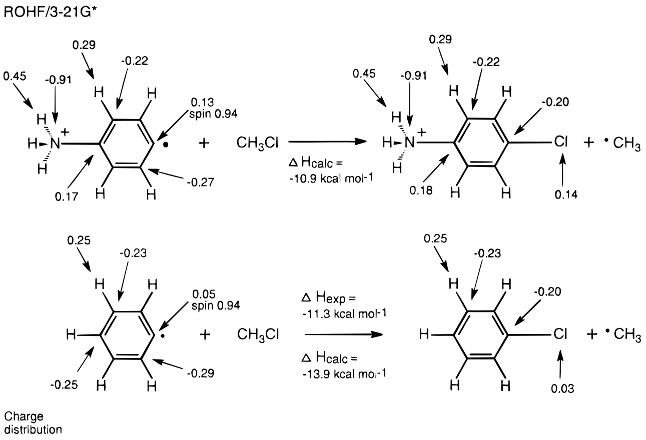
Scheme 8



Scheme 9

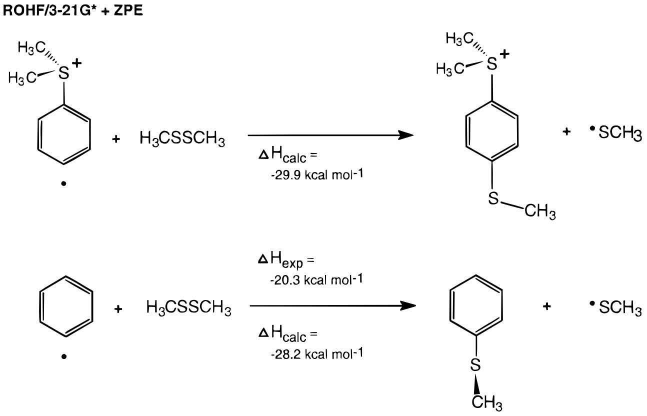


Table 3. Experimental Heats of Formation and Calculated Absolute Energies for the Reactants and Products of Two Chlorine Atom Transfer Reactions and Two Thiomethyl Transfer Reactions

molecule	ΔH_{exp} (kcal mol^{-1})	absolute energy (hartrees)[a]
p-$C_6H_4NH_3^{\bullet+}$	b	−283.73639
p-Cl-C_6H_4-NH_3^+	170[c]	−741.20053
C_6H_5Cl	13.0[c]	−686.15231
$C_6H_5^\bullet$	78.9[d]	−228.68348
CH_3Cl	−19.6[c]	−496.75847
$CH_3^\bullet$	35.0[d]	−39.31178
p-$(CH_3)_2SC_6H_4^{\bullet+}$		−702.26254
p-$(CH_3)_2S^+$-C_6H_4-SCH_3		−1137.36058
$C_6H_5SCH_3$	23.4[c]	−663.77878
CH_3SSCH_3	−5.8[c]	−870.05141
$CH_3S^\bullet$	29.4[c]	−435.00107

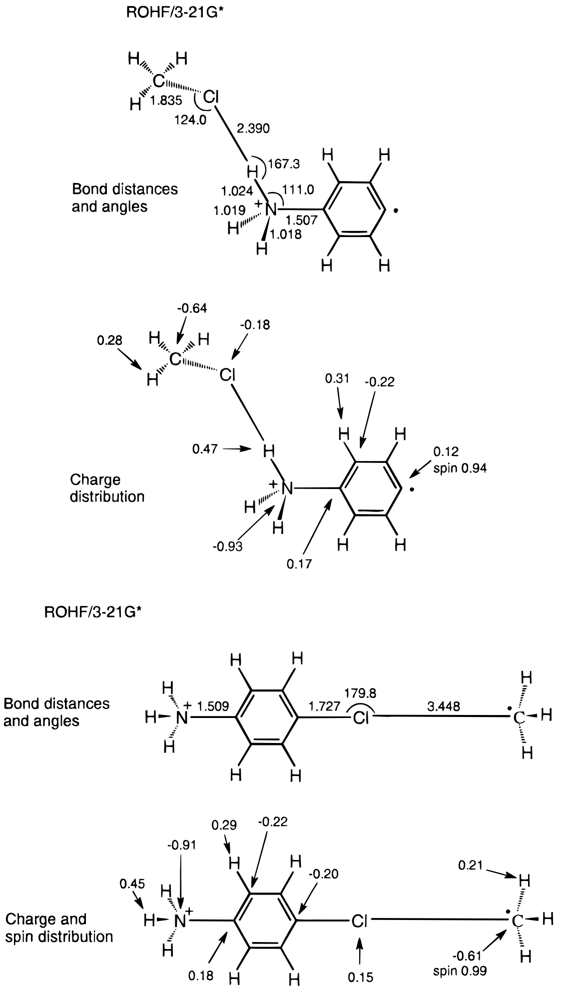
[a] Energy at the ROHF/3-21G* + ZPE level of theory. [b] Value not known. [c] Reference 26. [d] Reference 39.

Table 4. Calculated Absolute and Relative Energies of the Two Collision Complexes Shown in Scheme 10

molecule	absolute energy (hartrees)[a]	relative energy (kcal mol^{-1})
$CH_3Cl\cdots H_3N^+$-$C_6H_4^\bullet$	−780.51000	+1.6
H_3N^+-C_6H_4-$Cl\cdots CH_3^\bullet$	−780.51252	0

[a] Energy at the ROHF/3-21G* + ZPE level of theory.

Scheme 10



Conclusions

Gaseous phenyl radicals with different charged substituents are readily generated in the gas phase. The radicals with the charged group in the *meta* or *para* position are stable toward isomerization in spite of the prediction obtained from *ab initio* molecular orbital calculations that these species lie significantly higher in energy than their conventional isomers. The charge density was found to be localized at the substituent and the odd-spin density at the appropriate ring carbon in those charged phenyl radicals that were examined computationally.

The charged groups employed here do not directly participate in the reactions of the charged phenyl radicals. Further, the reactivity of these species is not a sensitive function of the type of charge site or size of the radical. However, decreasing the distance between the charge-bearing atom and the radical site increases the reaction efficiency toward electron-rich substrates. This finding is attributed to an increased electron deficiency at the radical site.

The chemical properties of the charged phenyl radicals were found to be markedly different from those of related conventional organic radical cations. However, the charged radicals show the same reaction pathways and similar reactivity trends toward different substrates as the neutral phenyl radical. These findings suggest that charged phenyl radicals with a chemically inert charge site provide a useful model for the mass spectrometric study of the properties of substituted phenyl radicals in the gas phase.

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