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Polarity of the Transition State Controls the Reactivity of Related Charged Phenyl Radicals Toward Atom and Group Donors

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Polar effects are demonstrated to be a key factor in controlling the reactivities of related charged phenyl radicals in different exothermic atom and group abstraction reactions in the gas phase. The effects of various *meta* substituents on the phenyl radicals' reactivity were probed via the measurement of bimolecular reaction rate constants by using Fourier transform ion cyclotron resonance mass spectrometry. This approach requires an additional, charged substituent to be present in the phenyl radical to allow mass spectrometric manipulation. The *m*-pyridinium group was chosen for this purpose. The substrates studied were allyl iodide, dimethyl disulfide, and *tert*-butyl isocyanide. Two of the reactions of interest, •I and $\bullet SCH_3$ transfer, are thought to occur by concerted bimolecular homolytic substitution (S_H2), and the third one, •CN transfer, by an addition/elimination mechanism. For all three substrates, the reaction rate was found to increase in the following order for the differently substituted phenyl radicals: $CH_3 \approx H < Br \approx Cl \approx COOH < NO_2 \approx CN$. This trend does not arise from differences in reaction exothermicities or bond dissociation energies but via lowering the reaction barrier by electronic effects. The stabilization of the transition state is attributed to its increased polar character. A semiquantitative measure of the barrier lowering effect for each substituent is obtained from its influence on the electron affinity of the charged radical, as the calculated (B3LYP/6-31+G(d)) adiabatic electron affinities of the radical model systems (ammonium instead of pyridinium charge site) follow the same trend as the reactivities.

Introduction

Phenyl radicals have been the focus of intense scrutiny in the gas phase as well as in solution.[1−3] However, few studies have been carried out to examine systematically the effects of substituents on reactions of phenyl radicals. The studies reported thus far have primarily focused on the effects of the *para* Cl, Br, and NO_2 substituents[4] on radical substitution and addition reactions.

In most instances, electron-withdrawing *para* substituents have been found to enhance radical substitution reaction rates. For example, Pryor et al.[4a] studied the rates of hydrogen abstraction by the *para* Br- and NO_2-substituted phenyl radicals and reported the following general reactivity trend: phenyl < *p*-bromophenyl < *p*-nitrophenyl radical. The rates were measured relative to chlorine abstraction from carbon tetrachloride. The above trend was found to apply to all the various hydrogen atom donors studied, including aromatic (e.g., thiophenol, toluene, ethylbenzene) and aliphatic compounds (e.g., acetone, cyclohexene, methyl acetate). Migita and co-workers[4c,d] demonstrated that this trend is not limited to hydrogen transfer reactions, as the electron-withdrawing *para* Cl and NO_2 substituents increase the rates of various reactions, including bromine abstraction from benzyl bromide and thiomethyl abstraction from dimethyl disufide.

Upon examination of polyhalogenated substrates, Migita and co-workers observed[4c,4d] a "reverse" substituent effect for hydrogen, bromine and chlorine atom abstraction from the polychlorinated substrates chloroform, bromotrichloromethane, and carbon tetrachloride, respectively. The *p*-nitro and *p*-chlorophenyl radicals undergo these reactions *more slowly* than the phenyl radical.[4d,e] This reversed substituent effect was attributed to a difference in the nucleophilicities of the substrates.[4c−e] Substrates with low nucleophilicities were rationalized to react more quickly with the fairly nonpolar phenyl radical than with the electrophilic *p*-nitrophenyl radical.[4c−e] These results were mirrored by da Silva Corrêa et al.,[4f]

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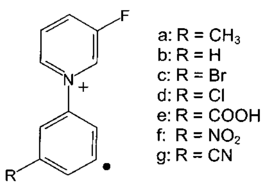
who discovered that the *p*-nitrophenyl radical undergoes chlorine atom abstraction from benzenesulfonyl chloride more slowly than its *p*-methoxy analogue. Further, Tilset et al.[4b] reported the reactivity order, *p*-methoxy > *p*-chloro > *p*-nitrophenyl radical, for hydrogen abstraction from acetonitrile relative to Br abstraction from dibromomethane.

Addition−elimination reactions appear to follow the same substituent effect trends as radical substitution reactions. For example, Migita et al.[4d,g] have reported that the *para* Cl and NO_2 substituents increase the rate of addition−elimination reactions of the phenyl radical with the substrates allyl methyl sulfide and allyl bromide. These addition reactions are followed by elimination of a thiomethyl or bromo radical, respectively. Arnaud and co-workers[4h] demonstrated that *para* Cl and NO_2 substituents on phenyl radicals increase the rate of homolytic arylation of the neutral 4-methylpyridine, but decrease the rate for the electron-poor 4-methylpyridinium ion. Similarly, Ito and co-workers[4j] reported the reactivity trend *para* NO_2 > Cl > phenyl radical > CH_3 > OCH_3 for homolytic arylation of nitrobenzene and chlorobenzene, while no trend was obvious for the homolytic arylation of toluene and anisole. The effect of electron-withdrawing substituents appears to be strongly dependent on the nature of the substrate.

Electron-withdrawing substituents appear to increase the phenyl radical's reaction rate for addition as well as radical substitution reactions, except for very electron-deficient substrates, for which the opposite trend applies. The most commonly accepted explanation for these trends involves lowering the energy of the transition state by increasing its polarity (polar effects) by a σ-acceptor (or σ-donor) substituent.[4a,c,d,f,h] However, the importance of enthalpic effects has not been rigorously addressed. Further, almost no data are available regarding the impact of *meta* substituents on the reactivity of phenyl radicals, despite the fact that *meta* substituents allow the examination of inductive effects separately from resonance effects. To improve general understanding of the properties of substituted phenyl radicals, including those that play a role in the action of antitumor and antiviral drugs,[5] we decided to systematically examine the intrinsic reactivity of *meta*-substituted phenyl radicals toward different types of compounds.

Our experimental approach is based on phenyl radicals with a chemically inert, positively charged group that allows their manipulation in the mass spectrometer.[6−8] The addition of various neutral substituents to the phenyl ring allows a systematic examination of substituent effects on the gas-phase reactions of the charged phenyl radicals.[8] We earlier demonstrated the feasibility of this approach in a study wherein the strongly electron-withdrawing fluoro substituent was shown to increase the hydrogen atom abstraction rate of phenyl radicals from several organic hydrogen atom donors.[8a] This finding is in agreement with the literature results described above. Further, the relative reactivities of the charged phenyl radicals toward the different hydrogen atom donors were found to follow the same trends as reported[9] for radicals in solution, e.g., phenol < thiophenol < benzeneselenol, thus providing further support for the general relevance of the information obtained in these studies. We recently employed the same approach to demonstrate that both *ortho* and *meta* F, Cl, CF_3, and CN (but not CH_3) substituents enhance a phenyl radical's ability to abstract an iodine atom from allyl iodide.[8b] We report herein an examination of substituent effects displayed by a series of *meta*-substituted charged radicals (Scheme 1) upon attack at iodine, cyano, and disulfide groups.

Scheme 1



Experimental Section

All experiments were carried out using an Extrel Model FTMS 2001 Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR). This instrument contains a differentially pumped dual cell aligned within the magnetic field produced by a 3.0 T superconducting magnet operated at about 2.8 T. The nominal base pressure was $<10^{-9}$ Torr, as maintained with two Balzers turbomolecular pumps (330 L/s), each backed with an Alcatel 2012 mechanical pump. The two cells are separated by a common wall (the conductance limit) which contains a 2 mm hole in the center. This plate and the other two trapping plates were maintained at +2 V unless otherwise stated.

All reagents were obtained commercially and used as received, with the exception of 1,3-diiodo-5-nitrobenzene, which was synthesized via a standard literature procedure.[10] Samples were introduced into the instrument by using a Varian leak valve, a heated solids probe, a set of pulsed valves,[11] or batch inlet systems equipped with variable leak valves. The nominal reagent pressures were measured with two ionization gauges, one located on each side of the dual cell.

Most of the charged phenyl radicals were generated using a procedure reported earlier.[6−8] The halobenzene precursors (3,5-dibromotoluene for **a**, 1-bromo-3-iodobenzene for **b**, 1,3,5-tribromobenzene for **c**, 1,3-dichloro-5-iodobenzene for **d**, 3-bromo-5-iodobenzoic acid for **e** and 1,3-diiodo-5-nitrobenzene for **f** and **g**; Scheme 2a and 2b) were introduced at a nominal pressure of 6.0×10^{-8} to 3.0×10^{-7} Torr into one side of the dual cell by using the Varian leak valve or the heated solids probe. 3-Fluoropyridine was added at approximately the same nominal pressure into the same cell through a batch inlet system. The mixture was subjected to electron ionization, which resulted in an intense signal for the halobenzene radical cation. This ion signal was maximized for each experiment (typically 20 eV electron energy, 5 μA emission current, and 30 ms ionization time). The halobenzene radical cation was allowed to react with the neutral 3-fluoropyridine present in the cell, leading to *ipso*-substitution of one of the halogen

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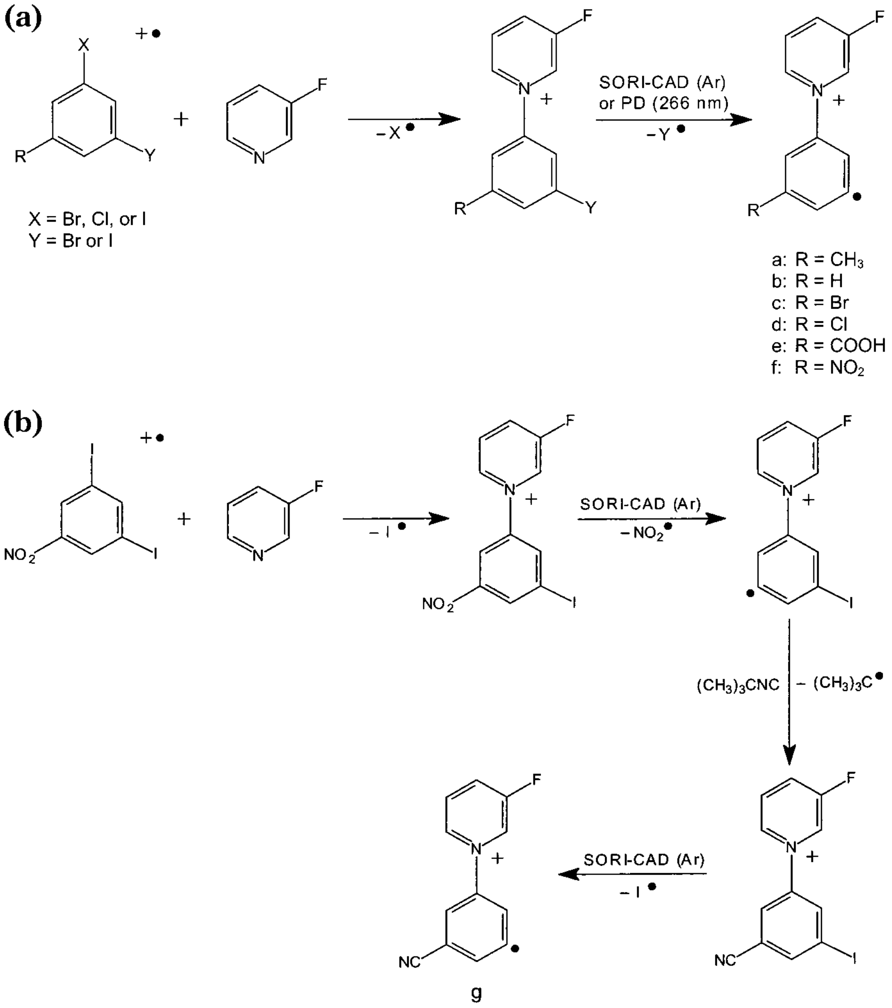
Scheme 2



atoms.[12] Depending on the system, formation of an abundant halogen displacement product occurred in 0.5−5 s.

The substituted halobenzene ions, generated in one side of the dual cell as described above, were transferred into the other side by grounding the conductance limit plate for approximately 140 μs (124−163 μs), which allowed the ions to pass through a 2 mm hole in this plate. The transferred ions were allowed to cool for 1 s by IR light emission and by collisions with the neutral molecules present in this cell (the reagent to be used in the final stage of the experiment). The substituted halobenzene ions were then isolated by applying a stored-waveform inverse Fourier transform (SWIFT)[13] excitation pulse to the plates of the cell. After isolation, the desired charged phenyl radicals **a**−**f** were formed by homolytic carbon−halogen bond cleavage in the substituted halobenzenes (Scheme 2a). Photodissociation[14a] was used to achieve carbon−bromine bond cleavage, while sustained off-resonance irradiated collision-activated dissociation (SORI-CAD)[14b] was employed to accomplish carbon−iodine and carbon−nitro bond cleavage. SORI-CAD was implemented by introducing argon into the cell via a pulsed valve assembly (the nominal peak pressure in the cell was approximately 1×10^{-5} Torr) and collisionally activating the ions with argon for 1 s at a frequency 0.5−1.0 kHz higher than the cyclotron frequency of the ions.[14b] The ions were then cooled for 1 s as described above. Photodissociation involved 5−10 pulses of a 266 nm Nd:YAG laser (10 Hz repetition rate) followed by cooling of the ions for 1 s by IR emission and by collisions with argon pulsed into the cell (peak pressure about 1×10^{-5} Torr).[14a]

The charged phenyl radical **g** was synthesized by using a variation of the procedure described above. An iodine-substituted charged phenyl radical was generated from 1,3-diiodo-5-nitrobenzene as described above (Scheme 2b**)**. The radical was then allowed to react with *tert*-butyl isocyanide (added into the same cell at a nominal pressure of approximately 1.2×10^{-7} Torr), to form an abundant •CN abstraction product. This species was subsequently subjected to a SORI-CAD event, which induced homolytic cleavage of the carbon−iodine bond to yield the CN-substituted charged phenyl radical **g.** The ions were cooled for 1 s as discussed previously.

The charged phenyl radicals were isolated as described above and allowed to react with a neutral reagent for a variable period of time (typically 0.5−20 s). Detection was carried out by using “chirp” excitation (124 V_{p-p} amplitude, 2.7 MHz bandwidth, 3.2 kHz/μs sweep rate). All spectra are the average of at least 30 transients and were recorded as 64k data points, subjected to one zero fill prior to Fourier transformation and background corrected by using a previously described procedure.[15]

Primary products were identified based on their fixed relative abundances (branching ratios) at short reaction times.

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The second-order rate constant of each reaction (k_{exp}) was obtained from a semilogarithmic plot of the relative abundance of the reactant ion versus time by assuming pseudo-first-order kinetics. The collision rate constant (k_{coll}) was calculated using a parameterized trajectory theory.[16] The reaction efficiencies are given by k_{exp}/k_{coll}. The accuracy of the rate constant measurements is estimated to be ±50%, while the precision is usually better than ±10%. The greatest uncertainty arises from pressure measurement in the cell. The pressure readings of the ion gauges (located remote from the cell) were corrected for the sensitivity of the ion gauges toward each neutral reagent[17] and for the pressure gradient between the cell and the ion gauge. The latter correction factor was obtained by measuring rates of reactions with known rate constants involving the neutral reagent of interest.

Molecular orbital calculations based on the density functional theory were performed using the Gaussian94 revision E3[18a] or the Gaussian98 revision A7[18b] suite of programs. Reaction exothermicities (0 K) were determined by fully optimizing the geometries of the reactants and products and calculating their energies at the B3LYP/6-31G(d) level of theory. All the optimized geometries were verified to correspond to potential energy minima by harmonic frequency calculations (no negative eigenvalues). Zero-point vibrational energies (ZPVE) were calculated from the B3LYP/6-31G(d) harmonic frequencies and scaled by a factor of 0.9804 to account for the systematic overestimation of the vibrational frequencies by the density functional theory.[18d] Adiabatic electron affinities were obtained by fully optimizing the geometries of the charged radicals and the corresponding zwitterions and calculating their energies and the zero-point vibrational energies at the B3LYP/6-31+G(d) level of theory. The direct calculation of the adiabatic electron affinity of a reference system, the neutral phenyl radical, provided a value, 1.06 eV, that is in good agreement with the experimentally determined[19] adiabatic electron affinity (1.1 eV).

Results

Generation of the Radicals. The charged phenyl radicals **a**−**f** (Scheme 1) were synthesized and purified by a multistep procedure described earlier in detail[6−8] (Scheme 2a). Generation of the charged phenyl radical **g** required a more involved synthesis. First, an iodine-substituted charged phenyl radical was produced using the method employed to generate the charged phenyl radicals **a**−**f** (Scheme 2b). This species was allowed to react with *tert*-butyl isocyanide in order to introduce the CN substituent (Scheme 2b). Finally, collisional activation[14b] using argon as a target gas was employed to induce homolytic cleavage of the carbon−iodine bond that generated the desired CN-substituted charged phenyl radical **g** (Scheme 2b).

Efficiencies of the Radical Abstraction Reactions. The charged radicals were allowed to react with allyl iodide, dimethyl disulfide, and *tert*-butyl isocyanide. The exclusive reaction for dimethyl disulfide and *tert*-butyl isocyanide was thiomethyl and cyano radical transfer, respectively. For allyl iodide, iodine atom abstraction was the main reaction pathway, but a small amount of allyl radical transfer was also observed (note that for allyl bromide, this is the major reaction pathway in solution[4g] and in our experiments[8c]). The temporal variation of reactant and product ion abundances was recorded. No secondary reactions were observed. The primary products and their branching ratios, together with the reaction efficiencies (eff = k_{exp}/k_{coll}), are given in Table 1. In each case, the charged phenyl radicals react to form products characteristic of the neutral phenyl radical.[1−4,8,20,21]

Addition of a neutral electron-withdrawing substituent to the phenyl ring (radicals **c**−**g**, Scheme 1) enhances the reactivity of the charged phenyl radical **b** toward all of the reagents studied. For example, radical **b** abstracts a thiomethyl group from dimethyl disulfide at an efficiency of 8% (i.e., approximately 8 out of every 100 collisions leads to a reaction; Table 1), while the NO_2-substituted radical **f** undergoes the same reaction at an efficiency of 63%. Similarly, radical **b** abstracts a cyano group from *tert*-butyl isocyanide much more slowly (19%) than the CN-substituted radical **g** (104%; Table 1). In contrast, the CH_3 substituent appears to have a slight lowering effect on the reaction efficiencies. For example, **b** and the CH_3-substituted radical **a** react with allyl iodide at efficiencies of 16% and ∼13% and with dimethyl disulfide at efficiencies of 8% and ∼2%, respectively (Table 1).

The 3-dehydropyridinium radical **h** (Scheme 3), wherein the positive charge is located directly in the same ring that carries the radical site, was found to react very rapidly with all three reagents. This radical reacts with allyl iodide (eff = 81%) and dimethyl disulfide (eff = 79%) even faster than the NO_2-substituted charged phenyl radical **f** (eff = 58% and 63%, respectively; Table 1).

Computational Results. The exothermicities of the radical abstraction reactions were explored computationally (B3LYP/6-31G(d) + ZPVE) by determining the heats of reaction for chlorine, thiomethyl, and cyano abstraction from allyl chloride, methyl disulfide, and *tert*-butyl isocyanide, respectively. Our earlier research demonstrates that allyl chloride is a good model for allyl iodide in these enthalpy calculations (closely similar exothermicities).[8b] The use of methyl disulfide instead of dimethyl disulfide in our calculations is justified by the fact that thiomethyl abstraction from dimethyl disulfide and methyl disulfide by the neutral phenyl radical are exothermic by about the same amount, −22.5 and −23.3 kcal/mol, respectively.[22] Our calculations yield a value of −23.9 kcal/mol

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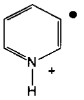
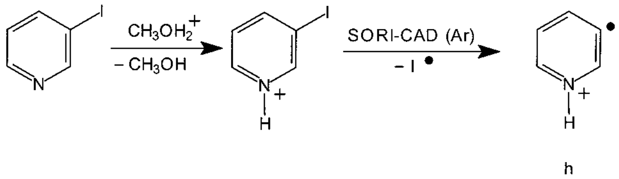
Table 1. Efficiencies[a] and Products[b] Measured for the Reactions of the Charged Phenyl Radicals a−h with Allyl Iodide, Dimethyl Disulfide, and *tert*-butyl Isocyanide

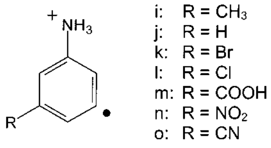
ion	R	allyl iodide	dimethyl disulfide	*tert*-butyl isocyanide
a	CH_3	•I abstraction (88%) •C_3H_5 abstraction (12%) eff ≈ 13%[c]	•SCH_3 abstraction (100%) eff ≈ 2%[c]	•CN abstraction (100%) eff ≈ 20%[c]
b	H	•I abstraction (91%) •C_3H_5 abstraction (9%) eff = 16%	•SCH_3 abstraction (100%) eff = 8%	•CN abstraction (100%) eff = 19%
c	Br	•I abstraction (91%) •C_3H_5 abstraction (9%) eff = 27%	•SCH_3 abstraction (100%) eff = 19%	•CN abstraction (100%) eff = 38%
d	Cl	•I abstraction (88%) •C_3H_5 abstraction (12%) eff = 23%	•SCH_3 abstraction (100%) eff = 23%	•CN abstraction (100%) eff = 31%
e	COOH	•I abstraction (85%) •C_3H_5 abstraction (15%) eff = 29%	•SCH_3 abstraction (100%) eff = 18%	•CN abstraction (100%) eff = 37%
f	NO_2	•I abstraction (84%) •C_3H_5 abstraction (16%) eff = 58%	•SCH_3 abstraction (100%) eff = 54%	•CN abstraction (100%) eff = 104%
g	CN	•I abstraction (91%) •C_3H_5 abstraction (9%) eff = 58%	•SCH_3 abstraction (100%) eff = 63%	•CN abstraction (100%) eff = 104%
h		•I abstraction (90% •C_3H_5 abstraction (10%)) eff = 81%	•SCH_3 abstraction (100%) eff = 79%	•CN abstraction (97%) HCN abstraction (3%) eff = 86%

[a] Reaction efficiency (eff) = $k_{\mathrm{exp}}/k_{\mathrm{coll}}$. [b] Relative product abundances are given in parentheses. [c] Isomerization of ~5% of ions to an unreactive form during the experiment causes a deviation from pseudo-first-order kinetics. The rate constant (k) was obtained by nonlinear regression on the best fit to a simple kinetic model ([ion] = ln(C exp($-kt$) − C + 1); C = fraction of reactive isomer) based on initial presence of two isomers; an equally good fit was obtained for isomerization during reaction.

Scheme 3



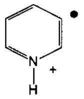
Scheme 4



for thiomethyl abstraction from methyl disulfide, in excellent agreement with the experimental value (−23.3 kcal/mol). Therefore, this level of theory appears suitable for our purposes. With the exception of the pyridium radical **h**, simple radical models, *meta* CH_3- (**i**), H- (**j**), Br- (**k**), Cl- (**l**), COOH- (**m**), NO_2- (**n**), and CN-substituted (**o**) 3-dehydroanilinium ions (Scheme 4), were employed in the calculations instead of the larger radicals examined experimentally. Justification for this approach is provided by our earlier work.[8a]

The reaction exothermicities were found to be insensitive toward substitution on the charged phenyl radical (Table 2). For example, the exothermicities for abstraction of a thiomethyl group from methyl disulfide and a cyano group from *tert*-butyl isocyanide by the radicals fall within the range 26.9−31.2 and 31.4−33.0 kcal/mol, respectively. Further, the slight variations in the exothermicities do not correlate with changes in the measured reaction efficiencies. For example, abstraction of a cyano group from *tert*-butyl isocyanide by radical **j** (R = H) is predicted to be slightly more exothermic (ΔH_{rxn} = −32.9 kcal/mol) than the same reaction involving the NO_2-substituted radical **n** (ΔH_{rxn} = −31.7 kcal/mol), but the reaction occurs more slowly for the experimentally studied radical **b** (R = H; 19%) than for its NO_2 substituent analogue **n** (104%). The reaction exothermicities for the 3-dehydropyridinium radical **h** are predicted to be slightly greater than those of the other radicals for the reactions with allyl chloride and methyl disulfide (1−3 kcal/mol) but lower for *tert*-butyl isocyanide (1−2 kcal/mol; Table 2). This variation is not only unlikely to be great enough to account for the dramatic differences in reaction efficiencies, but it also does not correlate with the observed reactivity trends. Radical **h** was found to react faster than the other radicals with all the three substrates and not just with those for which the reaction

Table 2. Calculated (Becke3LYP/6-31G(d)+ZPVE) Heats of Reaction (in kcal/mol) for •Cl Abstraction from Allyl Chloride, •SCH_3 Abstraction from Methyl Disulfide, and •CN Abstraction from *tert*-Butyl Isocyanide by the Charged Phenyl Radicals h−o

ion	R	allyl chloride	methyl disulfide	*tert*-butyl isocyanide
i	CH_3	−25.7	−26.9	−33.0
j	H	−25.9	−27.2	−32.9
k	Br	−25.5	−27.6	−32.4
l	Cl	−25.5	−27.5	−32.2
m	COOH	−25.7	−27.7	−32.0
n	NO_2	−25.7	−28.6	−31.7
o	CN	−25.8	−28.4	−31.8
h		−26.8	−31.2	−31.4

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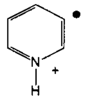
(22) (a) *NIST Standard Reference Data Base Number 69*; Mallard, W. G., Lindstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, August 1997 (http://webbook.nist.gov). (b) Leeck, D. T.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1994**, *29*, 106. (c) Li, W.-K.; Chiu, S.-W.; Ma, Z.-W.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1993**, *99*, 8440.

Table 3. Calculated (Becke3LYP/6-31+G(d)+ZPVE) Adiabatic Electron Affinities (in eV) for the Charged Radicals h−o

radical	R	adiabatic electron affinity (eV)
i	CH_3	5.11
j	H	5.22
k	Br	5.52
l	Cl	5.55
m	COOH	5.45
n	NO_2	5.90
o	CN	5.82
h		6.53

is estimated to be more exothermic. For example, abstraction of a cyano group from *tert*-butyl isocyanide by radical **h** and radical **j** (R = H) is calculated to be exothermic by 31.4 and 32.9 kcal/mol, respectively (Table 2), but radical **h** reacts more rapidly (86%) with this reagent than radical **b** (R = H; 19%; Table 1).

The effects of substituents on the adiabatic electron affinities of charged phenyl radicals[23] were also explored computationally (B3LYP/6-31+G(d); Table 3) by using the 3-dehydroanilinium radicals **l**−**o** as well as the 3-dehydropyridinium radical **h**. The presence of an electron-withdrawing *meta* Cl substituent in radical **l** increases the electron affinity of the charged radical by 0.33 eV relative to radical **j** (Table 3). This finding is supported by the results of Squires and co-workers, who reported that a *meta* Cl substituent increases the electron affinity of the neutral phenyl radical by 0.5 eV (1.1 vs 1.6 eV).[19] The NO_2-substituted radical **n** has a greater electron affinity (5.90 eV; Table 3) than any of the other substituted dehydroanilinium species examined computationally. The 3-dehydropyridinium radical **h** has the greatest electron affinity (6.53 eV; Table 3**)** of all the charged phenyl radicals studied.

Discussion

General Considerations on Radical Reactions of Gaseous Distonic Radical Cations. Gas-phase ion−molecule reactions that take place in high vacuum are free from solvation effects, with the exception of the initial solvation of the ionic reactant by the neutral reagent molecule. Ion−dipole and ion-induced dipole forces lower the potential energy of the gas-phase ion−molecule collision complex and provide energy to overcome moderate barriers on the reaction coordinate. For the systems discussed here, this energy lowering is estimated to be 6−7 kcal/mol on the basis of molecular orbital calculations. Substitution on the radical does not affect this energy, as demonstrated by examination of the radicals **b** and **g** (CN substituent) solvated by dimethyl sulfide (6 kcal/mol for **b** and 7 kcal/mol for **g**; B3LYP/6-31G(d)+ZPVE). The exact configuration of the collision complex also plays only a minor role, as calculations involving several different orientations between the ion and molecule revealed energy variations that were less than 2 kcal/mol.

Table 4. Selected Thermochemical Properties of the Neutral Reagents

neutral reagent	BDE (kcal/mol)a	IE (eV)[a]	μ_D (D)[b]
allyl iodide	44	9.27	1.56
dimethyl disulfide	65	8.1	1.94
tert-butyl isocyanide	92	10.5	4.34

[a] Ref 22. [b] Ref 26.

Exothermic and slightly endothermic reactions occur at observable rates in our experiments. The reaction rate (expressed as efficiency = percent of collisions resulting in reaction) is controlled by the energy difference (ΔE) between the isolated reactants and the bottleneck for reaction,[24] the transition state for atom/group transfer in this work. *Factors that decrease the energy of the transition state facilitate the reaction, just as in solution*. However, at some point upon lowering the transition state energy, ΔE becomes so large that the reaction occurs at collision rate (efficiency is 100%) and is insensitive to further barrier lowering effects.

Radical substitution reactions are often associated with substantial enough energy barriers that they do not occur at collision rate.[25] To observe these reactions in the gas phase, they usually have to be highly exothermic.[8] Iodine abstraction from allyl iodide and thiomethyl abstraction from dimethyl disulfide or methyl disulfide by the phenyl radical are all exothermic by 23 kcal/mol (these data are not available for *tert*-butyl isocyanide).[22] The analogous reactions for the charged phenyl radicals studied here were estimated to be exothermic by 28 ± 3 kcal/mol (based on simple model systems; B3LYP/6-31G(d) + ZPVE; Table 2) while CN abstraction from *tert*-butyl isocyanide was calculated to be slightly more exothermic (32 ± 1 kcal/mol). Therefore, these three types of reactions appeared suitably exothermic for our experimental study. The observed sensitivity of the reaction efficiencies to substitution (discussed below) demonstrates that ΔE is fairly small for these systems.

Several pieces of evidence rule out the possibility that the reactivity trends reported here and earlier[8] for differently substituted, gaseous charged phenyl radicals toward a specific reagent might be due to variables *other than barrier height*, such as gas-phase collision dynamics. For example, the trends observed in this work are independent of variations in the type, size, or polarity (Table 4) of the substrate. The results reported earlier[8b] for allyl iodide reactions demonstrate that the size of the radical and the size and location of its substituents are irrelevant (unless they affect the transition state energy). Finally, the limited amount of information available in the literature[4] on substituent effects for the neutral phenyl radical agree with our findings.

Reactions with Allyl Iodide and Dimethyl Disulfide. The electron-withdrawing *meta* substitutents were found to enhance the reactivity of the charged

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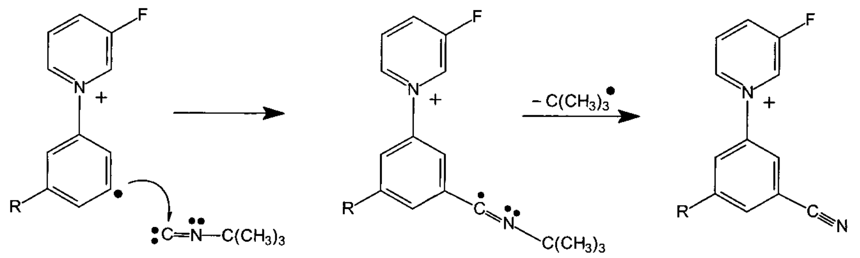
[23] The anions corresponding to the charged phenyl radicals, used in calculating the radicals' electron affinities, were determined to be singlets by calculating (at the Becke3LYP/6-31+G(d) level of theory) the vertical electron affinities of the 3-dehydropyridinium radical as it abstracts an electron to produce a singlet (EA = 6.12 eV) versus a triplet (EA = 5.21 eV) zwitterion (i.e., the singlet zwitterion is more stable than its triplet analogue by 21 kcal/mol). Vertical rather than adiabatic values were calculated since a ground-state geometry for the triplet analogue was not found.

[24] Barfknecht, A. T.; Dodd, J. A.; Salomon, K. E.; Tumas, W.; Brauman, J. I. *Pure Appl. Chem.* **1984**, *56*, 1809.

[25] See, for example: (a) Tedder, J. M. *Tetrahedron* **1982**, *38*, 313. (b) Sidebottom, H.; Treacy, J. *Int. J. Chem. Kinet.* **1984**, *16*, 579. (c) Shonkhai, S.; Whittle, R. *Int. J. Chem. Kinet.* **1984**, *16*, 543. (d) Fox, R. J.; Evans, F. W.; Szwarc, M. *Trans. Faraday Soc.* **1961**, *57*, 1915. (e) Alcock, W. G.; Whittle, E. *Trans. Faraday Soc.* **1965**, *61*, 244.

[26] McLellan, A. L., *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1989; Vol. 3

Scheme 5



phenyl radicals toward allyl iodide and dimethyl disulfide. The observed reactivity ordering for both substrates is $CH_3 < H < Br \approx Cl \approx COOH < NO_2 \approx CN$. These results are in qualitative agreement with solution findings that the electron-withdrawing *para* Br, Cl, and NO_2 substituents enhance the reactivity of neutral phenyl radicals toward bromine and thiomethyl abstraction from benzyl bromide and dimethyl disulfide, respectively.[4c,d]

A CH_3 substituent in the *meta* position does not significantly affect the reactivity of the charged phenyl radical **a**. This finding agrees with solution results; a *para* CH_3 substituent has a negligible influence on the rate of hydrogen atom abstraction from hydrogen atom donors such as acetone, hexane, and methyl acetate by the neutral phenyl radical.[4a,g]

Abstraction of a thiomethyl group from dimethyl disulfide and iodine atom from allyl iodide by a phenyl radical likely occurs by bimolecular homolytic substitution (S_H2) via a concerted backside displacement, similar to the S_N2 mechanism.[1,2a,4,20] The reactivity results indicate that the transition state energy for these reactions is lowered by electron-withdrawing substituents. This energy lowering is not attributable to changes in reaction enthalpy, since addition of an electron-withdrawing substituent to the phenyl ring increases the reaction efficiency without an associated increase in the reaction exothermicity (see computational results; Table 2). We conclude that the lowering of the reaction barrier is likely due to polar effects,[27] which are discussed in detail below.

Polar Effects in Reactions of the Charged Phenyl Radicals. The positively charged 3-fluoropyridinium substituent acts as a strongly electron-withdrawing group and causes all of the charged phenyl radicals examined here to be electrophilic, regardless of the additional neutral substituent present on the phenyl ring.[28] The energy of the transition state for an atom abstraction reaction involving an electrophilic radical and a substrate with a relatively low ionization energy, such as allyl iodide and dimethyl disulfide, is likely to be significantly influenced by the contribution of the following charge-transfer resonance structure (far right) to the electronic configuration of the transition state:[1,27,29,30]

$$[R^{\bullet}\ X-Y] \leftrightarrow [R-X^{\bullet}\ Y] \leftrightarrow [R^{-}\ X-Y^{+\bullet}]$$

The lower the ionization energy of the substrate X−Y, the lower the energy of the charge-transfer resonance structure $[R^{-}\ X-Y^{+\bullet}]$ and the greater its stabilizing influence on the transition state. The ionization energies of allyl iodide and dimethyl disulfide are 9.27 and 8.1 eV, respectively, (Table 4) and hence substantially lower than those of substrates for which the polar effect is reversed,[4c,4d] e.g., chloroform, IE = 11.37 eV. The charge-transfer resonance structure $[R^{-}\ X-Y^{+\bullet}]$ also is stabilized by an increase in the electron affinity of the radical $R^{\bullet}$; greater electron affinity leads to a more stable anion R^{-}, resulting in a lower-energy transition state.[1,27,30] Indeed, the charged phenyl radicals with the greater electron affinities (Table 3) react faster with allyl iodide and dimethyl disulfide (Table 1). In fact, *the observed reactivity trend* $CH_3 \approx H < Br \approx Cl \approx COOH < NO_2 \approx CN$ (**a** ≈ ***b*** < ***c*** ≈ ***d*** ≈ ***e*** < ***f*** ≈ ***g***) *exactly matches the electron affinity ordering calculated for the model systems* (***i*** ≈ ***j*** < ***k*** ≈ ***l*** ≈ ***m*** < ***n*** ≈ ***o***). This trend extends to the 3-dehydropyridinium radical **h**, whose exceedingly fast reactions are explained by an electron affinity (6.53 eV) that is substantially larger than those of the other radicals (5.22−5.90 eV; Table 3).

Reactions with *tert*-Butyl Isocyanide. The phenyl radical abstracts a cyano group from *tert*-butyl isocyanide in a process[9a] that likely involves radical attack at the terminal carbon of isocyanide to form an imidoyl radical intermediate (Scheme 5).[1,31] Substituent effects on these reactions have not been previously examined. Despite the different reaction mechanisms (addition to CN to form an intermediate vs concerted backside displacement), the substituent effects observed for reactions of the charged phenyl radicals with *tert*-butyl isocyanide are the same as for allyl iodide and dimethyl disulfide (Table 1). Again, the reaction efficiency trend cannot be rationalized by changes in the overall reaction exothermicities (Table 2) or exothermicities for addition (46.1 and 48.5 kcal/mol at B3LYP/6-31G(d) + ZPVE for **b** and **g**, respectively), but instead it follows the electron affinity ordering of the radicals (Table 3). Hence, polar effects appear to be the rate-controlling factor also for reactions with *tert*-butyl isocyanide.

The observation that *meta* substitutents have a significant impact on the efficiencies of the reactions of the charged phenyl radicals with *tert*-butyl isocyanide sug-

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[27] Pross, A. In *Theoretical and Physical Principles of Organic Reactivity*; John Wiley & Sons: New York, 1995.

[28] The charged phenyl radicals studied here are highly electrophilic, as demonstrated by a calculation on the interaction of the 3-dehydroanilinium radical **j** with *tert*-butyl isocyanide (Becke3LYP/6-31+G(d)). The energy required to transfer an electron from *tert*-butyl isocyanide to the 3-dehydroanilinium radical is drastically lower (5.5 eV) than that for transfer of an electron from **i** to *tert*-butyl isocyanide (13.7 eV.; based on adiabatic values).[1]

[29] Pross, A.; Yamataka, H.; Nagase, S. *J. Phys. Org. Chem.* **1991**, *4*, 135.

[30] Wong, M. W.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 6284.

[31] (a) Kim, S. S.; Yang, K. W.; Lee, C. S. *J. Org. Chem.* **1996**, *61*, 4827. (b) Kim, S. S.; Lee, K. S.; Hwang, S. B.; Kim, H. *Tetrahedron Lett.* **1990**, *31*, 3575. (c) Kim, S. S. *Tetrahedron Lett.* **1977**, *32*, 2741. (d) Blum, P. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1313. (e) Blum, P. M.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1976**, 535. (f) Davies, A. G.; Nedelec, J. Y.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 209. (g) Banks, R. E.; Haszeldine, R. N.; Stephens, C. W. *Tetrahedron Lett.* **1972**, *35*, 3699. (h) Danen, W. C.; West, C. T. *J. Am. Chem. Soc.* **1973**, *95*, 6872. (i) *Isonitrile Chemistry*; Ugi, I., Ed.; Academic Press: New York, 1971.

gests that addition of the charged phenyl radical to *tert*-butyl isocyanide rather than elimination of the *tert*-butyl group is the rate-limiting step in this reaction. The distance between the substituent and the site of bond cleavage during the elimination step is quite significant, and the substituent is expected to have little or no influence on the polar character of the transition state for this step (Scheme 5). However, the substituents have a similarly strong effect on the overall rate for all the three reactions studied. This can only be explained if addition to the isocyanide is the rate-controlling step. This result is supported by the conclusion made by Pross, Radom, and others[1,30] that radical addition transition states often possess substantial polar character. For example, Radom and co-workers used molecular orbital calculations to show that addition of the electrophilic $^{\bullet}CH_2CN$ radical to substituted alkenes is strongly influenced by polar effects.[30] Further, Migita et al.[4d,g] have reported that addition of the phenyl radical to allyl methyl sulfide and allyl bromide is facilitated by *para* Cl and NO_2 substituents on the radical.

Conclusions

Examination of the gas-phase reactivities of charged phenyl radicals toward allyl iodide, dimethyl disulfide, and *tert*-butyl isocyanide revealed an interesting trend, i.e., *all of these reactions are facilitated by meta substituents in the same order,* $CH_3 \approx H < Br \approx Cl \approx COOH < NO_2 \approx CN$. Traditional bond dissociation energy/enthalpy arguments do not adequately explain this trend, as the reaction exothermicities were computationally determined (B3LYP/6-31G(d)) to be independent of substitution. However, the reactivity trend matches the ordering of the radicals' electron affinities. Therefore, polarization of the transition state is concluded to be the rate-controlling factor in the reactions studied. This phenomenon is not limited to our special case of charged radicals. Similar findings have been made by Anderson, Clarke and Donahue[32] for *neutral* radical/molecule reactions. The electronic structures of the transition states for a large set of gas-phase radical-molecule reactions were reported to be so strongly influenced by valence bond configurations that are ionic rather than free radical in nature that estimates for barrier heights can be derived from purely ionic parameters of the system (EA of radical and IE of substrate or vice versa).[32]

Observations of polar effects on phenyl radical displacement reactions involving alkyl halides and disulfides have been reported in the literature,[4] while no knowledge exists concerning polar effects in radical reactions involving isocyanides. The reactivity trend found here parallels literature reports for substituent effects on hydrogen abstraction[4a] ($H < p\text{-}Br < p\text{-}NO_2$)[4a] and bromine and thiomethyl abstraction[4c,d] ($H < p\text{-}Cl < p\text{-}NO_2$) by neutral *para*-substituted phenyl radicals. These abstraction reactions likely occur by concerted backside displacement (S_H2 mechanism), similar to the S_N2 mechanism.[1,2a,4,20] However, cyano abstraction from isocyanides is thought[9] to involve radical attack at the terminal carbon of the isocyanide to form an imidoyl radical intermediate.[1,9] Neverheless, substituents on the charged phenyl radicals were found to impact the reactions with *tert*-butyl isocyanide exactly in the same way as the reactions with allyl iodide and dimethyl disulfide. This result suggests that addition of the radical to *tert*-butyl isocyanide is the rate-limiting step, rather than elimination of the *tert*-butyl radical from the adduct and that the addition step is susceptible to polar effects, very much like the radical displacement reactions. This finding is supported by Takayama et al., who reported that hydrogen atom abstraction and alkene addition reactions respond similarly to polar effects.[4g]

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JO001634R

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(32) (a) Donahue, N. M.; Clarke, J. S.; Anderson, J. G. *J. Phys. Chem. A* **1998**, *102*, 3923. (b) Clarke, J. S.; Kroll, J. H.; Donahue, N. M.; Anderson, J. G. *J. Phys. Chem.* **1998**, *102*, 9847.