J. Org. Chem. **2000,** *65,* 645−651

# Polar Effects on Iodine Atom Abstraction by Charged Phenyl Radicals

Jenny L. Heidbrink, Kami K. Thoen, and Hilkka I. Kenttämaa*

*Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393*

*Received September 21, 1998*

The ability of differently substituted charged phenyl radicals (a class of distonic radical cations) to abstract an iodine atom from allyl iodide was systematically examined in the gas phase by using Fourier transform ion cyclotron resonance mass spectrometry. The reaction products and second-order reaction rate constants were determined for several radicals that differ by the type and/or number of substituents located in the *ortho*- and/or *meta*-position with respect to the radical site. All the radicals also carry a *para*-pyridinium group needed for mass spectrometric manipulation. These electron-deficient phenyl radicals react with allyl iodide by predominant iodine atom abstraction. The reaction is facilitated by the presence of neutral electron-withdrawing substituents, such as F, $CF_3$, Cl, or CN. The extent of rate increase depends on the type and number of the substituents, as well as their location relative to the radical site. Based on molecular orbital calculations (PM3 and Becke3LYP/6-31G(d)+ZPVE), the indicated variations in the transition state energy are not related to enthalpic factors. Instead, the results are rationalized by polar effects arising from a variable contribution of a stabilizing charge transfer resonance structure to the transition state. A semiquantitative measure for the barrier-lowering effect of each substituent is provided by its influence on the electron affinity of the radical (the electron affinities were calculated by Becke3LYP/ 6-31+G(d) and AM1, which were found to produce similar values). Methyl substitution does not significantly affect the electron affinity, and accordingly, does not have a detectable effect on reactivity. Methyl groups located at *ortho*-positions are an exception, however. *o*-Methyl-substituted phenyl radicals undergo exothermic rearrangement to a benzyl radical in competition with iodine abstraction from allyl iodide.

## Introduction

The reactions of the phenyl radical have been extensively investigated in solution and in the gas phase.[1−4] However, the knowledge on substituted phenyl radicals appears to be limited to reactions of the *p*-Cl-, *p*-Br-, *p*-$NO_2$-, *p*-$CH_3$-, and/or *p*-$OCH_3$-substituted radicals with bromine (benzyl bromides, $CH_2Br_2$, $CBrCl_3$) and chlorine atom donors ($CCl_4$), various hydrogen atom donors, disulfides, and substituted propenes, as well as 4-methylpyridine and its protonated form.[5] These studies have led to the general conclusion that the relatively nonpolar phenyl radical is converted into an electrophilic radical by Cl, Br, and $NO_2$ substituents, i.e., the substituted radicals react faster than the phenyl radical with atom donors with additional electron-donating substituents (e.g., benzyl bromide) and slower with those carrying electron-withdrawing substituents (e.g., $CBrCl_3$). On the other hand, the apparent “polarity” of a phenyl radical can be strongly dependent on the substrate, as demonstrated by the finding that the *p*-Cl-, *p*-$NO_2$-, and *p*-$CH_3$-substituted phenyl radicals behave as nucleophilic radicals toward the 4-methylpyridinium ion but as electrophilic radicals toward 4-methylpyridine.[5h] A more in-depth understanding of these substituent effects is desirable, considering the importance of substituted phenyl radicals in reactions ranging from organic synthesis to the action of antitumor and antiviral drugs.[1]

Gas-phase ion chemistry has proven to be a powerful tool for the study of many ionic reaction intermediates that are difficult to study in solution. This approach can be extended to reactive neutral species via ions that

---

(1) See for example: (a) *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Vol. 1. (b) *Free Radicals in Organic Chemistry*; Fossey, J., Lefort, D., Sorba, John Wiley & Sons: New York, 1995. (c) *Theoretical Aspects of Physical Organic Chemistry*; Shaik, S. S., Schlegel, H. B., Wolfe, S., Eds.; John Wiley & Sons: New York, 1992. (d) *Theoretical and Physical Principles of Organic Reactivity*; Pross, A., Ed.; John Wiley & Sons: New York: 1995.

(2) See for example: (a) Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754−3764. (b) Bridger, R. F.; Russell, G. S. *J. Am. Chem. Soc.* **1963**, *85*, 3765−3766. (c) Pryor, W. A.; Guard, H. *J. Am. Chem. Soc.* **1964**, *86*, 1150−1152. (d) Fu, J.-J. L.; Bentrude, W. G. *J. Am. Chem. Soc.* **1972**, *94*, 7710−7722. (e) Levy, A.; Meyerstein, D.; Ottolenghi, M. *J. Phys. Chem.* **1973**, *77*, 3044−3047. (f) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589−7600. (g) Scaiano, J. C.; Stewart, L. C., *J. Am. Chem. Soc.* **1983**, *105*, 3609−3614. (h) Yu, T.; Lin, M. C.; Melius, C. F. *Int. J. Chem. Kinet.* **1994**, *26*, 1095−1104. (I) Radziszewski, J. G.; Nimlos, M. R.; Winter, P. R.; Ellison, B. *J. Am. Chem. Soc.* **1996**, *118*, 7400−7401.

(3) Matimba, H. E. K.; Crabbendam, A. M.; Ingeman, S.; Nibbering, N. M. M., *J. Chem. Soc., Chem. Commun.* **1991**, 644−645.

(4) For gas-phase studies, see for example: (a) Fahr, A.; Stein, S. E. *J. Phys. Chem.* **1988**, *92*, 4951−4955. (b) Chen, R. H.; Kafafi, A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1418−1423. (c) Kopinke, F.-D.; Zimmerman, G.; Anders, K. *J. Org. Chem.* **1989**, *54*, 3571−3576. (d) Yu, T.; Lin, M. C. **1994**, *98*, 9697−9699. (e) Yu, T.; Lin, M. C. *J. Phys. Chem.* **1995**, *99*, 8599−8603.

(5) For substituted phenyl radicals, see: (a) Pryor, W. A.; Echols, J. T., Jr.; Smith, K. J. *J. Am. Chem. Soc.* **1966**, *88*, 1189−1199. (b) Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.* **1966**, *88*, 5534−5537. (c) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 2731−2738. (d) Takayama, K.; Kosugi, M.; Migita, T. *Chem. Lett.* **1973**, 193−195. (e) Takayama, K.; Kosugi, M.; Migita, T. *Chem. Lett.* **1973**, 215−218. (f) Migita, T.; Nagai, T.; Abe, Y. *Chem. Lett.* **1975**, 543−546. (g) Migita, T.; Takayama, K.; Abe, Y.; Kosugi, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1137−1142. (h) Arnaud, R.; Bonnier, J. M.; Fossey, J. *Nouv. J. Chimie* **1980**, *4*, 299−305. (i) Tilset, M.; Parker, V. *Acta Chem. Scand. B* **1982**, *36*, 123−124. (J) da Silva Correa, C. M. M.; Oliveira, M. A. B. C. S.; de Lurdes S. Almeida, M.; Rodrigues, P. C. M.; Fonseca, M. M. B.; Estrada, J. M. A. C. *J. Chem. Soc., Perkin. Trans 2* **1989**, 1643−1646. (k) Hazlewood, C.; Davies, M. J.; Gilbert, B. C.; Packer, J. E. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2167−2174.

10.1021/jo981911i CCC: $19.00

contain the reactive group of interest, as well as a remote, chemically inert charged group for mass spectrometric manipulation. Various intermediates have been studied this way, including the *o*- and *m*-benzynes,[6] phenylcarbenes,[7] and phenylnitrene.[7b] We have applied this approach to phenyl radicals via distonic radical cations[8,9] (ionized ylides, biradicals, and zwitterions) with a phenyl radical site and a chemically inert, positively charged substituent in the *meta*- or *para*-position.[10,11] The reactivity of these species was found to parallel that of the phenyl radical, i.e., the same reaction products and similar reactivity trends were observed with different substrates. The *N*-(4-dehydrophenyl)pyridinium ion, for example, undergoes[10b] radical reactions characteristic of the phenyl radical.

Inspired by the above results, we decided to examine whether the *N*-(4-dehydrophenyl)pyridinium ion can be employed to systematically study substituent effects on phenyl radicals' reactions. Iodine abstraction from allyl iodide was selected as the first reaction for study since the phenyl radical readily abstracts iodine atoms from various aromatic and aliphatic substrates.[12] Further, the rate of iodine abstraction by the phenyl radical from iodobenzenes has been found to depend on the substitution of the substrate, which indicates sensitivity to polar effects.[12] Hence, the iodine atom abstraction ability of the charged phenyl radical may be sensitive to its substituents, and thus provide a means to improve our fundamental understanding of atom abstraction reactions.

## Experimental Section

All experiments were performed using a dual-cell Extrel Model 2001 Fourier transform ion cyclotron resonance mass spectrometer (FT/ICR) described previously.[6,11] Allyl iodide and halogenated benzenes with various additional substituents (1,4-diiodobenzene, 1-chloro-3-(trifluoromethyl)-4-iodobenzene, 1-chloro-2-(trifluoromethyl)-4-iodobenzene, 5-bromo-2-iodotoluene, 2-bromo-5-iodotoluene, 1-bromo-3-chloro-4-iodobenzene, 5-bromo-2-iodo-*m*-xylene, and 1-chloro-2-cyano-4-nitrobenzene), as well as 3-iodopyridine, were obtained commercially and used as received. Electron ionization mass spectrometry did not reveal impurities in these materials. The halogenated neutral precursors were introduced at a nominal pressure of $(1.0-1.5) \times 10^{-7}$ Torr into one side of the dual cell by using a heated solids probe or a variable leak valve. The appropriate nucleophile (pyridine or 3-fluoropyridine for **1**−**10**) or protonating agent (methanol for **11**) was added into the same cell (nominal pressure of about $2 \times 10^{-7}$ Torr) through a batch inlet system containing an Andonian leak valve. The mixture was subjected to electron ionization (typically 20 eV electron energy, 8 $\mu$A emission current, 50 ms ionization time), which resulted in an abundant signal for the halobenzene radical cation. The radical cation was allowed to react with pyridine or 3-fluoropyridine (for **11**, ionized methanol and its fragment ions were allowed to protonate 3-iodopyridine) to produce the desired halogen displacement product (typical reaction times were 500 ms−10 s).

The ions formed upon the halogen displacement reaction were transferred into the other side of the dual cell by grounding the conductance limit plate for approximately 150 $\mu$s and cooled for one second by allowing irradiative emission and collisions with the neutral molecules present in this cell (the reagent to be used in the final stage of the experiment). The ions were isolated by ejecting all unwanted ions from the cell through the application of a stored-waveform inverse Fourier transform[13] (SWIFT) excitation pulses to the excitation plates of the cell (Extrel SWIFT module). Cleavage of the remaining carbon−halogen or carbon−nitrogen bond was accomplished by collisional activation with argon target (pulsed into the cell at a peak nominal pressure of $6 \times 10^{-6}$ to $1 \times 10^{-5}$ Torr). The sustained off-resonance irradiation[14] (SORI) technique was used to kinetically excite the ions (about one second irradiation at a frequency 0.5−1.0 kHz higher than the cyclotron frequency of the ions). The product ions (charged phenyl radicals) were kinetically and internally cooled by giving them time ($\geq 0.4$ s) for radiative emission and for collisions with the neutral molecules present in this cell. This approach was found to yield the same results (reaction products and rate constants) as obtained by using a high-pressure burst of argon (pulsed into the cell at a peak nominal pressure of about $10^{-5}$ Torr), which indicates sufficient cooling of the ions.

The charged phenyl radicals were isolated by ejecting all other ions from the cell, as described above, and allowed to undergo reactions with allyl iodide (nominal pressure approximately $1.1 \times 10^{-7}$ Torr; introduced by using a batch inlet containing an Andonian leak valve) for a variable period of time (typically 1−20 s). All ions were excited for detection by using a "chirp" excitation sweep of 2.65 MHz bandwidth and 3200 Hz/$\mu$s sweep rate. All the measured spectra are the average of at least 30 transients and were recorded as 64 K data points subjected to one zero fill prior to Fourier transformation.

In the experiments described above, the neutral reagent is present at a great excess relative to ions. This leads to pseudo-first-order kinetics. The second-order rate constant ($k_{\text{reaction}}$) of each ion−molecule reaction was obtained from a semilogarithmic plot of the relative abundance of the reactant ion versus time. The collision rate constants ($k_{\text{coll}}$) were calculated using a parameterized trajectory theory.[15] The reaction efficiencies are given by $(k_{\text{reaction}}/k_{\text{coll}}) \times 100\%$. 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 allyl iodide[16] and for the pressure gradient between the dual cell and the ion gauge. Both correction factors were obtained by measuring rates for electron-transfer reactions of allyl iodide that can be expected to occur at collision rate due to their high exothermicity.[17] Internal consistency between correction factors obtained by examining different radical

---

(6) Thoen, K. K.; Kenttämaa, H. I. *J. Am. Soc.* **1999**, *121*, 800−805.

(7) (a) Hu, J.; Hill, B. T.; Squires, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 11699−11700 and references therein. (b) Wenthold, P. G.; Hu, J.; Hill, B. T.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1998**, *179/180*, 173−183 and references therein.

(8) (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929−2931. (b) Bouma, W. J.; McLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930−2931. (c) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931−2932.

(9) (a) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123−202. (b) Stirk, K. M.; Kiminkinen, M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649−1665.

(10) (a) Smith, R. L.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1995**, *117*, 1393−1396. (b) Thoen, K. K.; Smith, R. L.; Nousiainen, J. J.; Nelson, E. D.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1996**, *118*, 8669−8676. (c) Leeck, D. T.; Stirk, K. M.; Zeller, L. C.; Kiminkinen, L. K. M.; Castro, L. M.; Vainiotalo, P.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1994**, *116*, 3028−3038.

(11) Li, R.; Smith, R. L.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1996**, *118*, 5056−5061.

(12) (a) Danen, W. C.; Saunders *J. Am. Chem. Soc.* **1969**, *91*, 5924−5925. (b) Danen, W. C.; Tipton, T. J.; Saunders: D. G. *J. Am. Chem. Soc.* **1971**, *93*, 5186−5189. (c) Danen, W. C.; Winter, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 716−720.

(13) Chen, L.; Wang, T.-C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1987**, *59*, 449−454.

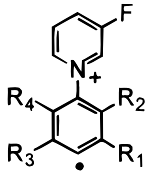
(14) Gauthier, J. W.; Trautman, T. R.; Jacobson, D. B. *Anal. Chim. Acta* **1991**, *246*, 211−225.

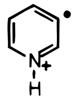
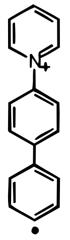
(15) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183−5185.

(16) (a) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149−153. (b) Miller, K. J.; Savchick, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206−7213.

(17) (a) Han, C.-C.; Wilbur, J. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1992**, *114*, 887−893 and references therein. (b) Richardson, D. E. *J. Phys. Chem.* **1986**, *90*, 3697−3700. (d) Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513.

**Table 1. Efficiency ($k_{reaction}/k_{coll}$) of Reaction of Allyl Iodide with Differently Substituted Phenyl Radicals**



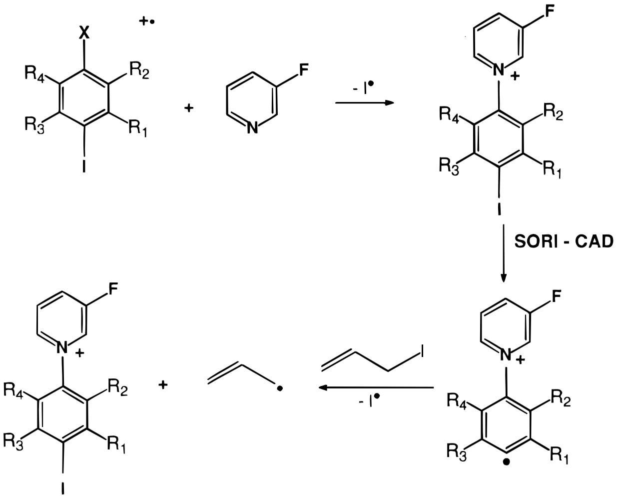
| | Reactant ion | | | | Reaction Efficiency | Branching Ratio (%) | | Absolute |
|---|---|---|---|---|---|---|---|---|
| Ion | R1 | R2 | R3 | R4 | ($k_{reaction}/k_{coll}$) | I• Abstraction | Allyl Abstraction | I• transfer Efficiency |
| **1** | H | H | H | H | 11% | 94 | 6 | 10% |
| **2** | $CH_3$ | H | H | H | 7%[a] | 100 | 0 | 7% |
| **3** | H | $CH_3$ | H | H | 12% | 94 | 6 | 11% |
| **4** | $CH_3$ | H | $CH_3$ | H | 6%[a] | 100 | 0 | 6% |
| **5** | $CF_3$ | H | H | H | 26% | 93 | 7 | 24% |
| **6** | H | $CF_3$ | H | H | 17% | 100 | 0 | 17% |
| **7** | Cl | H | H | H | 21% | 75 | 25 | 16% |
| **8** | F | H | H | H | 29% | 85 | 15 | 25% |
| **9** | F | F | F | F | 45% | 70 | 30 | 32% |
| **10** | H | CN | H | H | 26% | 91 | 9 | 24% |
| **11** | |  N+ H | | | 66% | 90 | 10 | 59% |
| **12** | |  N+ | | | 2% | 97 | 3 | 2% |

[a] The reaction displayed nonpseudo-first-order kinetics. Efficiencies were obtained by fitting the data with a nonlinear curve-fitting program that models the decay of the ion on the basis that the ion is rearranging within the collision complex.

cation reagents supports the validity of the measurements (e.g., with $CS_2^{+\bullet}$ and the acetone radical cation). Each reaction spectrum was background corrected by using a previously described procedure.[10,11]

The Spartan and the Gaussian 92 Revision F suites of programs[18] were used to carry out the molecular orbital calculations. Either a semiempirical method (usually AM1; PM3 was used for calculations involving iodine) or the density functional theory (Becke3LYP/6-31G(d)) was used to fully optimize the geometries of all radicals. The optimized structures were verified to correspond to an energy minimum by calculating the harmonic vibrational frequencies (no imaginary frequencies). The relative energies obtained from the density functional calculations were corrected by adding the zero point vibrational energy calculated at the same level of theory. The electron affinities calculated for the phenyl radicals are vertical values, i.e., the relative energies of the reduced radicals (carbanions or zwitterions) were calculated as single points by using the optimized geometries of the corresponding radicals (obtained either by AM1 or Becke3LYP6-31G+(d)).

**Scheme 1**



## Results and Discussion

**Synthesis of the Charged Radicals.** Various derivatives of the *N*-(4-dehydrophenyl)pyridinium ion (Table 1) were formed using a recently developed[6,11] multistep procedure in a dual-cell Fourier transform ion cyclotron resonance mass spectrometer. The first step involves the generation of a substituted haloiodo- or halonitrobenzene radical cation by electron ionization. *Ipso*-substitution[10,11,19] of an iodine, chlorine, or bromine atom with pyridine or 3-fluoropyridine yields the desired substituted iodo- or nitrobenzene ion. Collision-activated dissociation induced by sustained off-resonance irradiation[14] forms the desired charged phenyl radical by cleavage of an iodine atom or a nitro group (see Scheme 1). The radical **11** was formed by protonating 3-iodopyridine and then collisionally cleaving the iodine atom. The charged radicals were then isolated for reactivity studies. The purpose of using the fluorinated nucleophile was to enable distinction between the brominated radical cation precursor and the substitution product (bromine and

---

(18) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gil, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA 1992.

(19) (a) Thölmann, D.; Grützmacher, H.-F. *J. Am. Chem. Soc.* **1991**, *113*, 3281−3287. (b) Thölmann, D.; Grützmacher, H.-F. *Org. Mass Spectrom.* **1989**, *24*, 439−441.

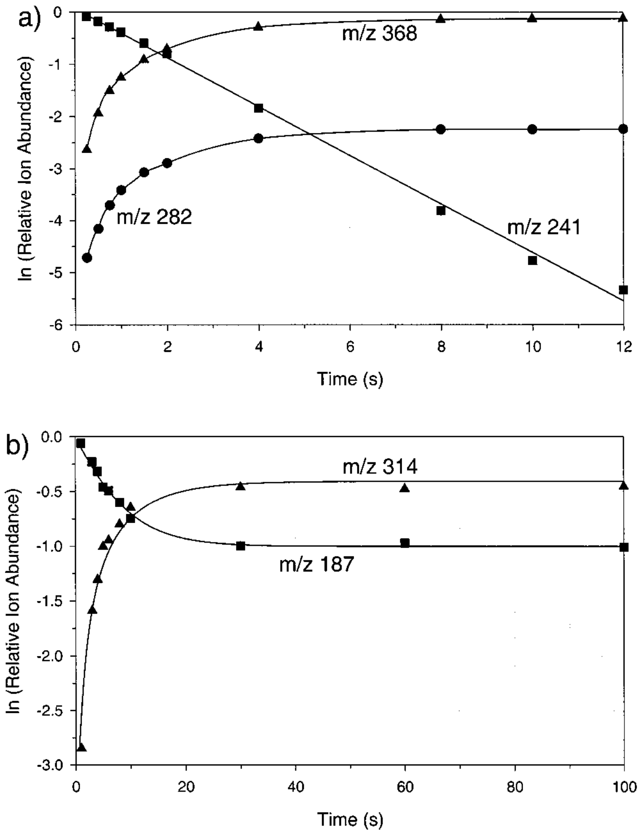
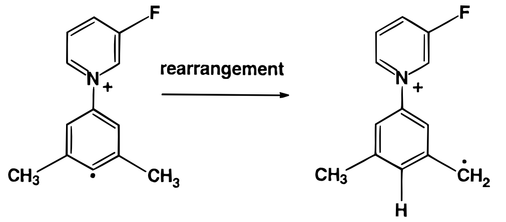


**Figure 1.** Temporal variation of the reactant and product ion abundances for the reaction of allyl iodide with (a) the *o*-$CF_3$-substituted charged phenyl radical **5** (*m*/*z* 241; iodine abstraction: *m*/*z* 368; allyl abstraction: *m*/*z* 282), and (b) with the *o*-$CH_3$-substituted charged phenyl radical **2** (*m*/*z* 187; iodine abstraction: *m*/*z* 314). The data points are connected with arbitrary smooth lines except for b (see Table 1). For part a, the decay of the reactant ion is presented with a linear least-squares fit.

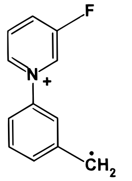
### Scheme 2



pyridine have the same MW, 79 amu). The fluorine substituent does not affect the iodine atom abstraction efficiency of these charged phenyl radicals, as indicated by the same reaction efficiency (10%) measured for both the *N*-(4-dehydrophenyl)pyridinium ion and the *N*-(4-dehydrophenyl)-3-fluoropyridinium ion (**1**).

The time dependences of the relative abundances of the reactant and product ions show that the reactions of the *N*-(4-dehydrophenyl)-3-fluoropyridinium ion and most of its derivatives obey *pseudo*-first-order kinetics, as expected (excluding **2** and **4**, Table 1; Figure 1a). This finding, combined with prior evidence[10] that the isomeric *ortho*-, *meta*-, and *para*-substituted charged phenyl radicals do not interconvert, suggests that the radical populations are likely to be isomerically pure.

However, reactions of the radicals **2** and **4**, each with methyl groups adjacent to the radical site, do not follow pseudo-first-order kinetics (Figure 1b). This observation is readily understood if the radicals, within the collision complex, undergo partial rearrangement to more stable benzyl radicals in direct competition with the iodine atom abstraction. An incomplete rearrangement (resulting in a mixture of isomeric radicals) would lead to deviation from pseudo-first-order kinetics if the rearranged $\pi$-radical (Scheme 2) reacts with allyl iodide at a different rate than the unrearranged $\sigma$-radical. The authentic charged benzyl radical **13** (generated from the radical cation of



**13**

3-chlorobenzyl bromide by the same method as the phenyl radicals) was found to be unreactive toward allyl iodide, in support of the proposed rearrangement. The observation of deviation from pseudo-first-order kinetics for the *o*-$CH_3$- substituted radicals but not for their *meta*-isomers suggests that the isomerization occurs without active participation by allyl iodide, e.g., it does not involve reversible hydrogen atom transfer involving allyl iodide. However, the solvation energy provided by allyl iodide appears to be necessary to drive the reaction, since complete isomerization was never observed, and the population of reactive and unreactive isomers was constant and reproducible from one experiment to another.

**General Considerations on Radical Reactions of Gaseous Distonic Radical Cations.** Only exothermic reactions are observed under the conditions employed in this study. Reaction efficiencies (fraction of collisions that leads to reaction) of gas-phase ion−molecule reactions are generally governed[20a] by the difference in energy between the separated reactants and the transition state ($\Delta E$ in Figure 2a). Variations in reaction efficiencies due to substituents can only be observed with this experimental approach provided that this energy gap is small. If the central barrier (transition state energy) is too low, i.e., 5−10 kcal/mol below the energy of the separated reactants, the efficiency will approach unity (every collision leads to reaction).[20a] On the other hand, if the central barrier is too high, the efficiency will become too low to measure (a few kcal/mol above the energy of the separated reactants is too high for the systems studied here).

Atom abstraction reactions of radicals are often associated with energy barriers that prevent them from proceeding at collision rate.[21] For these reactions to be observable in high vacuum, they usually must be highly exothermic.[11,22] Iodine abstraction from allyl iodide by phenyl radical is such a reaction (the enthalpy change[23] is −23 kcal/mol). Hence, allyl iodide was selected as the substrate for the present study. Since the same neutral

---

[20] (a) Barfknecht, A. T.; Dodd, J. A.; Salomon, K. E.; Tumas, W.; Brauman, J. I. *Pure Appl. Chem.* **1984**, *56*, 1809−1818. (b) Gas-Phase Ion Chemistry; Bowers, M. T., Ed.; Academic Press: London, 1979; Vol. I.

[21] See, for example: (a) Tedder, J. M. *Tetrahedron* **1982**, *38*, 313−329. (b) Sidebottom, H.; Treacy, J. *Int. J. Chem. Kinet.* **1984**, *16*, 579−590. (c) Shonkhai, S.; Whittle, R. *Int. J. Chem. Kinet.* **1984**, *16*, 543−558. (d) Fox, R. J.; Evans, F. W.; Szwarc, M. *Trans. Faraday Soc.* **1961**, *57*, 1915−1927. (e) Alcock, W. G.; Whittle, E. *Trans. Faraday Soc.* **1965**, *61*, 244−254.

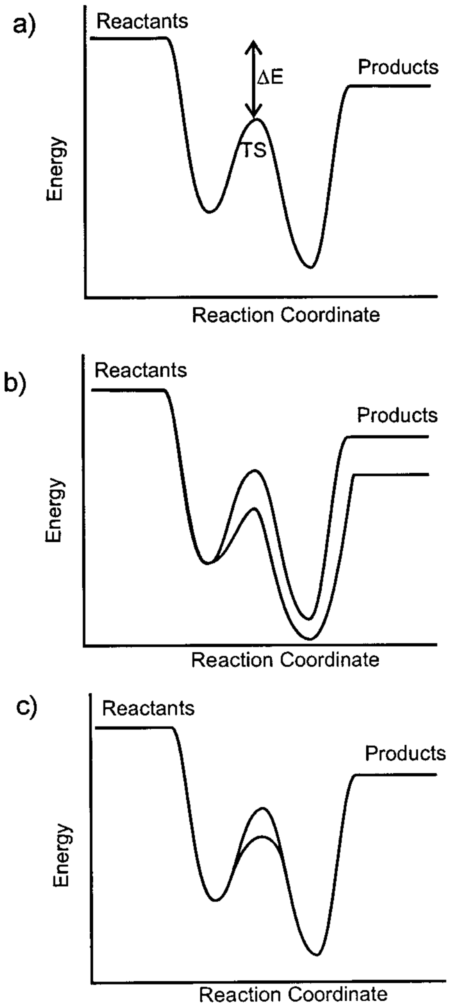
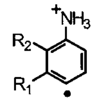
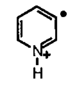
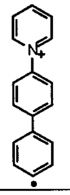


**Figure 2.** (a) A typical potential energy surface for an exothermic gas-phase ion−molecule reaction. The reaction rate is controlled by the energy difference between the isolated reactants and the transition state. (b) A schematic potential energy surface illustrating the lowering of the transition state energy due to increasing reaction exothermicity (c) and due to polar effects.

reagent was employed in all experiments and the only variable was substitution of the charged radical, trends in the measured reaction efficiencies can be expected to reflect changes in the barrier height (Figures 2b and 2c) rather than the stability[20b] of the initial gas-phase collision complex.

**Table 2. Computational Exothermicities ($\Delta H_{reaction}$ (kcal/mol)) for the Abstraction of a Halogen Atom by Model Charged Phenyl Radicals from Allyl Iodide (PM3) and Allyl Chloride (DFT)**

| Radical | $R_1$ | $R_2$ | $^{\bullet}$I abstraction[a] from allyl iodide | $^{\bullet}$Cl abstraction[b] from allyl chloride |
|---|---|---|---|---|
|  | H | H | -24.1 | -26.2 |
| | Cl | H | -21.8 | -25.5 |
| | $CF_3$ | H | -18.4 | -24.5 |
| | F | H | -23.7 | -27.0 |
| | H | CN | -24.4 | -26.0 |
| | H | $CH_3$ | -23.9 | -26.2 |
| | H | $CF_3$ | -23.4 | -26.2 |
| **11**  | NA | | -28.2 | c |
| **12**  | NA | | -22.1 | c |

[a] PM3 calculations. [b] Becke3LYP/6-31G(d) + ZPVE. [c] Not calculated.

**Reaction Efficiencies.** All the phenyl radicals studied react with allyl iodide by predominant iodine atom abstraction, presumably due to the high exothermicity of the reaction (the homolytic C−I bond dissociation energy of this substrate is only 44 kcal/mol).[23] An addition/elimination pathway leading to allyl abstraction is slow (≤ 15%) or not detectable for all but two cases (Table 1). Although hydrogen atom abstraction from allyl iodide is slightly more exothermic (~−28 kcal/mol) than iodine abstraction (see discussion below; Table 2), hydrogen abstraction was not observed. This finding is likely explained by the greater polarizability and the lower homolytic bond dissociation energy of the C−I bond (analogous C−H bond: ~75 kcal/mol, PM3). Analogous reactivity trends have been reported[21b,d,e] for simple carbon-centered radicals toward abstraction of different atoms (for $CH_3^{\bullet}$ and $CF_3^{\bullet}$, the trend is $Cl < H \sim Br < I$).

The *N*-(4-dehydrophenyl)pyridinium ion (**1**) abstracts iodine atom from allyl iodide at a reaction efficiency of 10% (10 collisions from 100 lead to iodine abstraction; **Table 1**); this value is used as the reference in the following discussion. The radicals **5**−**10**, with either an *o*-Cl, *o*-F, or *o*-$CF_3$ substituent, a *m*-$CF_3$ or *m*-CN substituent, or two *o*- and two *m*-F substituents, undergo iodine abstraction at a greater efficiency than **1** (16−32% vs 10%; Table 1). The *m*-$CH_3$- substituted radical **3** reacts at about the same efficiency as **1** (11%). The two *o*-$CH_3$-substituted radicals **2** and **4** react at a slightly lower efficiency.

**Reaction Exothermicities.** The observation of changes in the reaction efficiency upon introduction of additional substituents into **1** suggests that the iodine atom abstraction barrier must be close to the energy level of the isolated reactants and that electron-withdrawing substituents stabilize the transition state. Atom transfer barriers are controlled by avoided curve crossings.[1] The barrier is usually expected to be found at or below the crossing of two potential energy surfaces that correspond to a breaking and a forming bond. Therefore, the factor considered to be most important in determining the barrier height is the strength of the breaking and the forming bond (the Bell−Evans−Polanyi principle) (Figure 2b).[1,21a] A similar conclusion is reached by using the widely used valence bond model,[1c,d] which is based on the avoided crossing of the bonding and antibonding states of the reactants and products, with a perturbation by ionic excited states. Based on these theories, the most likely explanation for the observed variations in reaction efficiency is a varying strength for the newly formed

---

[22] Smith, R. L.; Chyall, L. J.; Stirk, K. M.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1993**, *28*, 1623−1631.

[23] NIST Standard Reference Data Base Number 69; Mallard, W. G., Lindstrom, P. J., Eds.; August 1997, National Institute of Standards and Technology: Gaithersburg MD, 20899 (http://webbook.nist.gov).

carbon−iodine bond (all reactions involve cleavage of the same bond).

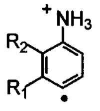
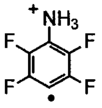
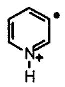
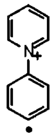
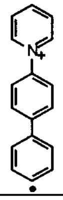
Molecular orbital calculations were carried out to estimate the effects of substitution on the reaction enthalpy. The calculations were performed on simple model systems, the 4-dehydroanilinium ion analogues (with an ammonium instead of a pyridinium charge site). Analogous results were obtained for iodine and chlorine abstraction reactions (Table 2). Abstraction of a chlorine atom from allyl chloride by radicals with an additional *o*-Cl, *o*-F, or *o*-$CF_3$ or a *m*-CN, *m*-$CH_3$, or *m*-$CF_3$ substituent was calculated to be highly exothermic, and the exothermicity was found to be nearly independent of substitution (−25 to −27 kcal/mol; Becke3LYP/6-31G(d) + ZPVE). Similarly, the enthalpy change of iodine atom abstraction from allyl iodide was calculated to be insensitive to substitution. The reaction of the 4-dehydroanilinium ion and its *o*-F, *o*-Cl and *m*-CN, *m*-$CH_3$, and *m*-$CF_3$ derivatives was estimated to be associated with a large negative enthalphy change (−22 to −24 kcal/mol; PM3) of the same magnitude as for the reaction of the phenyl radical with allyl iodide (experimental value is −23 kcal/mol;[23] −22 kcal/mol was calculated by PM3). Varying the substitution on the charged phenyl radical does not appear to lead to such changes in reaction enthalpy that would correlate with the differing reaction efficiencies. This is perhaps not surprising, considering the great exothermicity of the reaction in question.[1b,d,21a]

**Polarity of the Transition State.** The fact that the observed substituent effects do not arise from variations in reaction enthalpy suggests that polar effects[1a,b,d,21a,24,25] play a critical role in controlling the reaction efficiency of the charged radicals, i.e., the neutral substituents lower the energy of the transition state by enhancing its polar character (Figure 2c). Due to the polarizability of halogen atoms, halogen atom transfer reactions have been predicted to be more sensitive to polar effects than, for example, hydrogen atom abstraction.[21b,25] Examination of iodine abstraction by the nucleophilic methyl radical from $CF_3I$ and $CH_3CH_2I$ has demonstrated the importance of polar effects in these iodine transfer reactions: despite the same exothermicity, the reaction with $CF_3I$ is associated with a 3 kcal/mol lower barrier (4.3 kcal/mol) than the reaction with $CH_3CH_2I$.[21b]

According to Donahue et al.,[26] the barrier formation in many gas-phase radical abstraction reactions is best described as an avoided crossing of the ground state and an ionic excited state of the reactants and products. This is even more likely to be the case for the charged radicals studied here. The transition states of their reactions are polarized by an ionic configuration that corresponds to formal transfer of an electron from the neutral substrate to the radical. Hence, the observed variations in barrier heights are expected to arise primarily from differences in the radicals' electron affinities.[26]

The electron affinities (EA) of several charged phenyl radicals were estimated computationally. The adiabatic EA value of the 4-dehydroanilinium ion is calculated to be 5.10 eV (Becke3LYP/6-31+G(d) + ZPVE) and hence significantly greater than that of the phenyl radical (experimental EA = 1.1 eV;[23] we calculate the same value by Becke3LYP/6-31+G(d) + ZPVE). This finding suggests that polar effects may play a significantly greater role in controlling the reaction rates of the charged phenyl radicals than those of the phenyl radical. An even greater adiabatic EA of 6.53 eV is calculated for the 3-dehydropyridinium ion (**11**) with the charge distributed over the $\pi$-system of the same ring that contains the $\sigma$-radical site. The high EA is likely to be the origin of the great iodine abstraction efficiency measured for this radical upon interaction with allyl iodide (59%).

**Table 3. Vertical Electron Affinities (eV) Calculated for Model Charged Phenyl Radicals**

| Radical | $R_1$ $R_2$ | AM1 | Becke3LYP/6-31+G(d) |
|---|---|---|---|
|  | H H | 4.66 | 4.67 |
| | $CH_3$ H | 4.59 | 4.57 |
| | Cl H | 4.93 | 5.14 |
| | $CF_3$ H | 5.30 | 5.22 |
| | F H | 5.03 | 5.29 |
| | H CN | 5.12 | 5.23 |
| | H $CH_3$ | 4.61 | 4.52 |
| | H $CF_3$ | 5.21 | 5.01 |
|  | NA | 5.94 | a |
| **11**  | NA | 6.21 | 6.12 |
|  | NA | 4.47 | a |
| **12**  | NA | 3.07 | a |

[a] Not calculated.

Variation of EA with substitution of the 4-dehydroanilinium ion was examined by calculating vertical rather than adiabatic electron affinities because this is not only more straightforward but is also in better agreement with the curve crossing model.[1c,d,26] The vertical electron affinities of the radicals studied follow the same trend as the adiabatic ones, but their absolute value is smaller by a constant amount (0.4 eV), e.g., the vertical EA's obtained for the phenyl radical, the 4-dehydroanilinium ion and the 3-dehydropyridinium ion are 0.61, 4.67, and 6.12 eV, respectively (Becke3LYP/6-31+G(d)). Vertical EA values were estimated for a series of substituted 4-dehydroanilinium ions by using the semiempirical AM1 method as well as Becke3LYP/6-31+G(d) (Table 3). These two approaches give similar results that in most cases agree within 0.1 eV (e.g., 4-dehydroanilinium ion: 4.66 and 4.67 eV; 3-dehydropyridinium: 6.21 and 6.12 eV).

---

(24) Pross, A.; Yamataka, H.; Nagase, S. *J. Phys. Org. Chem.* **1991**, *4*, 135−140.

(25) Nieto, J. D.; Herrera, O. S.; Lane, S. I., Oexler, E. V. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 821−825.

(26) (a) Donahue, N. M.; Clarke, J. S.; Anderson, J. G. *J. Phys. Chem. A*, **1998**, *102*, 3923−3933. (b) Clarke, J. S.; Krill, J. H.; Donahue, N. M.; Anderson, J. G. *J. Phys. Chem. A* **1998**, *102*, 9847−9857.

The effect of replacing the pyridinium with the $NH_3^+$-group in the model systems was probed by calculating the vertical EA for one of the experimentally studied radicals, radical **1**. The value obtained (4.47 eV; AM1) is 0.2 eV smaller than that calculated for its model system, the 4-dehydroanilinium ion (EA = 4.66 eV). Hence, the $NH_3^+$-group appears to increase the EA of the phenyl radical more than a pyridinium charge site. However, both groups cause about a 5-fold increase in the EA of the phenyl radical and polarize the transition state for iodine abstraction in the same way. Therefore, the model system is expected to yield useful information on the observed reactivity trends.

In general, the computational results show an increase in the EA of the charged radical upon addition of electron-withdrawing substituents, i.e., at least qualitatively, EA appears to correlate with the iodine abstraction efficiency. For example, the reactivity trend $o$-$CF_3$ > $o$-Cl > $o$-H (efficiencies are 24%, 16%, and 10%, respectively) follows the trend obtained for the EA values of the analogous model systems (5.22, 5.14, and 4.67 eV, respectively; Becke3LYP/6-31+G(d)). Note that the increase in reaction efficiency caused by addition of an $o$-Cl or $o$-$CF_3$ substituent cannot be rationalized by enthalpic control since this substitution is associated with a *decrease* in reaction exothermicity.

To test the importance of EA in controlling the iodine abstraction barrier height, the radical **12** was included in this study. In this phenyl radical, the charged pyridinium substituent is separated by a phenyl ring from the radical-bearing phenyl. The EA of **12** is calculated to be drastically smaller (3.07 eV at AM1) than that of any of the other charged radicals studied. However, the estimated exothermicity of iodine abstraction is comparable to those calculated, for example, for the $o$-Cl- and $o$-$CF_3$-substituted 4-dehydroanilinium radicals (PM3: −22.1 vs −21.8 and −18.4 kcal/mol, respectively). Therefore, consideration of enthalphic factors alone suggests similar reactivity for radical **12** and the other two radicals. However, the ionic curve crossing model[26] predicts radical **12** to be less reactive than the others. This is what was observed, i.e., the radical **12** abstracts iodine from allyl iodide at a fraction of the efficiency measured for the $o$-Cl- and $o$-$CF_3$- substituted radicals **5** and **7** (2% vs 24 and 17%, respectively).

Relative EA values can also be used to rationalize the trends observed in reaction efficiencies upon variation of the location and the number of the neutral substituents. For example, the observation of a greater iodine atom abstraction efficiency for the $o$-$CF_3$-substituted radical **5** than for the isomeric *meta*-substituted radical **6** (24% and 17%, respectively) is readily explained by the greater electron affinity of the *ortho*-substituted radical (Becke3LYP/6-31+G(d) gives EA = 5.22 eV for the $o$-$CF_3$-substituted 4-dehydroanilinium ion and 5.01 eV for the *meta*-substituted isomer). An increase in the number of the substituents also increases EA, as indicated by the greater electron affinity (5.94 eV; AM1) calculated for the 2,3,5,6-tetrafluoro-4-dehydroanilinium ion than that of the $o$-F analogue (5.03 eV; AM1). Indeed, the radical **9** with four fluorine substituents reacts at a significantly greater efficiency (32% iodine abstraction efficiency) than the radical **8** with only one $o$-fluorine substituent (25% iodine abstraction efficiency).

Calculations yield EA values of 4.59 and 4.61 eV (AM1) for the 3-methyl- (*ortho*-) and 2-methyl-4-dehydroanilinium ions, respectively. These values are similar to that of the unsubstituted system (4.66 eV). Hence, based on the ionic curve crossing model, methyl substitution is not expected to greatly affect the reactivity of the radical. In agreement with this prediction, the radical with a $m$-$CH_3$ substituent (**3**) was found to react at the same efficiency (within experimental precision) as the unsubstituted radical **1** (11% and 10%, respectively).

However, it should be noted here that although $CH_3$ groups adjacent to the radical site (**2** and **4**) do not influence the polarity of the iodine abstraction transition state, they affect the reactivity of the phenyl radical in other ways. For example, steric hindrance is likely to partially explain the lower reaction efficiencies of these radicals (7% and 6%, respectively) as compared to **1** (10%). Further, as discussed above, the presence of a nearby $CH_3$ group apparently opens up a thermodynamically favorable rearrangement channel that competes with iodine abstraction within the collision complex with allyl iodide.

## Conclusions

The ability of the *N*-(4-dehydrophenyl)pyridinium ion to abstract an iodine atom from allyl iodide was found to be sensitive to substitution, and specifically, be enhanced by the presence of electron-withdrawing substituents. Qualitatively, the observations made here for iodine abstraction by charged phenyl radicals under gas-phase conditions parallel those made in solution for chlorine and bromine atom abstraction from electron-donating substrates (e.g., benzyl bromide) by the phenyl radical and its electrophilic $p$-Cl, $p$-Br, and $p$-$NO_2$ derivatives (and are reverse to those observed with electron-accepting polychlorinated substrates, e.g., $CCl_4$, $CBrCl_3$).[5] Further, in agreement with the slightly nucleophilic character reported for the $p$-$CH_3$-substituted phenyl radical in solution,[5a] we find that introduction of a methyl substituent into the *meta*-position in the charged phenyl radical does not change its iodine atom abstraction rate. On the basis of our observations, the *N*-(4-dehydrophenyl)pyridinium ion appears to provide a useful tool for probing substituent effects. However, our findings also suggest that polar effects may play a significantly greater role in controlling the reaction rates of charged phenyl radicals than those of the phenyl radical.

The results presented here underline the importance of *the ionic surface* in controlling the barrier height in radical atom abstraction reactions, as discussed by Donahue et al. in several recent publications.[26] The observed reactivity trends, and hence barrier heights, do not reflect changes in reaction enthalpy. Instead, the observations are readily rationalized by considering an avoided curve crossing that involves interaction of the ground state and an ionic excited state of the reactants. Accordingly, the electron affinity of the radicals is demonstrated to play a crucial role in controlling their iodine abstraction efficiency.

**Acknowledgment.** We thank the National Science Foundation (CHE-9710456) for financial support of this work. Mr. Hui Lui is thanked for performing some experiments.

JO981911I