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Charge-Site Effects on the Radical Reactivity of Distonic Ions[†]

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The perturbation on the intrinsic reactivity of a radical moiety by the presence of a nearby charged moiety was probed by comparing the reactivity of analogous positively and negatively charged distonic ions. The possible contributions of various factors (collisional encounter probability, ion−molecule solvation effects, reaction exothermicity, polar effects) to the overall perturbation are discussed. The *N*-(3-dehydrophenyl)-pyridinium and 3-dehydrobenzoate ions were chosen as distonic ion models of the phenyl radical for this study. The significant differences in their reaction rates are examined and the origins of these rate differences are explored. Observations that nucleophilic radicals react more rapidly with electron-deficient reagents and electrophilic radicals react more rapidly with electron-rich reagents can be made slightly more quantitative by comparing certain thermochemical values of each distonic ion (radical moiety IE and EA) with those of each neutral reagent. The smaller the relevant IE−EA energy difference, the lower the transition state energy and the faster the reaction. The overwhelming control of the transition state energy by the charge site of the distonic phenyl radical analogues described here emerges as an important caveat to their use as models for phenyl radical reactivity.

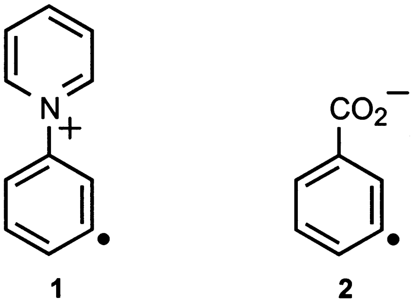
Introduction

The classification of "distonic ions" is often applied to a special subset of radical ions that possess spatial separation between charged and radical moieties.[1] A radical ion can be considered a distonic ion if it can be formed conceptually by the ionization of a biradical, zwitterion, or ylide.[2] Intuition suggests that, like their neutral forms (i.e., biradicals, zwitterions, and ylides), distonic ions should be high-energy species. Yet, distonic ions can be surprisingly stable—often lying lower in energy than their more conventional isomers (i.e., ions with the same connectivity as stable neutral molecules).[2] In many cases, this causes distonic ions to be formed by the spontaneous isomerization of such "conventional" radical ions.[3]

Distonic ions that possess a rigid bonding framework between their ionic and free radical moieties can often react fairly independently at each moiety. The reactions of these distonic ions can thus be thought of as a combination of the reactivities expected for the analogous ions and free radicals. For this reason, certain distonic ions have been used as models of radical and biradical species that can be studied via powerful mass spectrometric techniques.[4] These techniques often allow studies that would be difficult for the neutral analogues[4a] and provide useful information about the reactivity of such species.

This work explores the validity of the assumption that carefully selected distonic ions can serve as models for the chemical reactivity of radicals and biradicals. The perturbation on the intrinsic reactivity of the radical moiety by the presence of the nearby charged moiety was probed by comparing the reactivity of analogous positively and negatively charged distonic ions. Two distonic ion models of the phenyl radical were chosen for this study—the *N*-(3-dehydrophenyl)pyridinium (**1**) and 3-dehydrobenzoate (**2**) ions (Scheme 1).

SCHEME 1



Despite the immediately obvious differences in the identity and charge of the ionic moieties of **1** and **2**, these ions also have significant similarities. Both ions have the same radical moiety, and have their charged moiety located at the *meta*-position with respect to the radical sites.[5] This geometric configuration results in charged and radical moieties being held rigidly apart such that moderately sized neutral reagents will be unable to interact simultaneously with both charged and radical moieties. Reactions involving the participation of both charged and radical moieties will thus not be observed.[6] Further, both the *N*-phenylpyridinium and benzoate ions (the ionic frameworks that these two distonic ions are built on) are stable ions of low reactivity. Thus, the reactions of both distonic ions should arise exclusively from the phenyl radical moieties without direct participation of the charge sites.

The distonic ions **1** and **2** possess similar relative orientations of charged and radical moieties. Since the charged groups that perturb the intrinsic phenyl radical reactivity in these two cases are of opposite polarity, they should exert an opposite perturbation on the intrinsic reactivity of the phenyl radical. Thus, comparison of their reactivity serves to define the range of effects caused by the presence of a remote charge site. Both ions **1** and **2** have been generated and their reactivity studied previously.[4c,7] However, these studies were performed under different conditions and without any significant overlap of content. This work represents the first direct comparison of the

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reactivities of these analogous distonic phenyl radical ions. The significant differences in their reaction kinetics are examined and the origins of these rate differences are explored.

Experimental Section

The Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer used in these studies is a modified Finnigan Model 2001 FTMS described previously.[4c] Briefly, this instrument consists of two identical cubic cells (a "dual cell") in a vacuum chamber, lying within the bore of a 3 T superconducting magnet operated at 3.01 T. The common trapping plate between the two cells is part of a wall that divides the vacuum chamber in half. A 2 mm diameter hole in the center trap plate provides the only interruption in the wall. The two sides of the vacuum chamber (and thus the two cell regions) are independently pumped by two diffusion pumps (750 L/s) backed by mechanical pumps. Solid, liquid, and gaseous neutral reagents can thus be introduced independently into either cell region via various inlets, and the relative amounts present can be determined by ionization gauge pressure readings.

All compounds were used as obtained from the manufacturer. Allyl isophthalic acid was synthesized by partial hydrolysis of diallyl isophthalic acid. The product was purified by recrystallization. The identity of the allyl isophthalic acid was confirmed by mass spectrometry.

The *N*-(3-dehydrophenyl)pyridinium ion was synthesized in the mass spectrometer from the appropriate precursors (pyridine and 1,3-diiodobenzene) by using procedures reported previously.[4c] Chloride, generated by dissociative electron attachment from CCl_4 (2 eV ionization energy, 500 ms ionization time, 5 μA), deprotonates the allyl isophthalic acid to form the allyl isophthalate anion. This ion was transferred into the analyzer cell and subjected to two events of sustained off-resonance irradiation for collision-activated dissociation (SORI−CAD)[8] to eliminate the carboxylate moiety as carbon dioxide, and then an allyl radical, to generate the 3-dehydrobenzoate anion.

The charged phenyl radicals were isolated by stored-waveform inverse Fourier transform (SWIFT)[9] ejection of the unwanted ions. The isolated ions were subsequently allowed to react with a static pressure of neutral molecules for a variable length of time. Excitation for detection was accomplished by using a fast broadband sweep (from 2 kHz to 3 MHz, 200 V peak-to-peak, 2000 Hz/μs). The obtained time domain signal was subjected to Hanning apodization, followed by augmentation of the data set by an equal number of zeroes. All mass spectra are the average of ∼15 scans and the result of 64k data points/scan. Background correction was accomplished by subtraction of a mass spectrum obtained under identical conditions except that the charged phenyl radical of interest was ejected via a SWIFT waveform before reaction.

The second-order rate constants for the reactions were obtained from a plot of the relative abundance of the reactant ion versus time. The reaction efficiency is given as the ratio of the experimental second-order reaction rate constant to the theoretical collision rate constant that was estimated by using a parametrized trajectory theory.[10] Correction for the pressure gradient between the cell and the ion gauges and for the ion gauge sensitivity for each neutral reagent was accomplished by comparing measured rates of reaction with known reaction rate constants.

The calculations reported in this work were carried out by using the Gaussian 98 suite of programs[11] and performed at the B3LYP/6-31+G(d) + ZPVE level of theory. All of the calculated geometries of the molecules correspond to stationary points on their potential energy surfaces and do not possess imaginary frequencies. The vertical ionization energies and electron affinities were obtained from single-point calculations of the ground-state species.

Results

Synthesis and structural characterization of the *N*-(3-dehydrophenyl)pyridinium ion (**1**) has been presented previously.[4c] The structure of the 3-dehydrobenzoate ion (**2**) was characterized as follows. Low-energy collision-activated dissociation of this ion yielded an ion of *m*/*z* 76 exclusively. Formation of the ion of *m*/*z* 76 is consistent with loss of the carboxylate moiety of **2** as CO_2, yielding the 3-dehydrophenide ion. Further characterization of the ion of *m*/*z* 76 was aided by an investigation by DePuy and Squires on the reactivity of highly basic anions with CS_2.[12,13] The 3- and 4-dehydrophenide ions (but not the 2-dehydrophenide ion) were observed to react with CS_2 by two sequential sulfur atom abstractions to produce dithiobenzophenone radical anions.[13] Indeed, the ion of *m*/*z* 76, formed by CAD of **2**, reacts to completion with CS_2 by a sulfur atom abstraction to form a lone primary product of *m*/*z* 108 corresponding to the 3-dehydrothiophenoxide ion. A small amount of the dithiobenzophenone radical anion (*m*/*z* 140) also was produced at long reaction times. Differentiation between the 3- and 4-dehydrophenide ions was accomplished by reaction with nitrobenzene. The electron affinity of nitrobenzene is 1.00 ± 0.06 eV.[14] Consequently, nitrobenzene should be able to abstract an electron from the 3-dehydrophenide ion (EA = 0.85 ± 0.01 eV[7]), but not from the 4-dehydrophenide ion (EA = 1.265 ± 0.008 eV[15]). All of the ions of *m*/*z* 76 were found to react with nitrobenzene to form the nitrobenzene radical anion, indicating that the entire ion population of *m/z* 76 consists of 3-dehydrophenide ions.

Despite the extreme difference in the polarity of their charged moieties, the common phenyl radical moiety gives the two distonic ions **1** and **2** qualitatively similar reactivity in many cases. For example, they both display the characteristic radical reactivities of hydrogen atom abstraction from tetrahydrofuran and acetone, and bromine or iodine atom abstraction from molecular bromine and iodine as well as from various halogenated organic molecules (Table 1). The rates of these reactions range from the collision rate (i.e., reaction efficiency of 1.0) to more than 4 orders of magnitude lower than this benchmark rate (i.e., reaction efficiency of <0.0001). These latter rates approach the smallest measurable rates under these experimental conditions (i.e., ∼0.000 01). In several cases, no reaction rate was measurable for one of the two ions, and the reaction efficiency was assumed to be less than 0.000 01.

Regardless of the fact that **1** and **2** commonly undergo similar reactions, the efficiencies of their reactions often differ drastically (Table 1). For example, a dramatic difference in reaction efficiency is seen in the case of bromotrichloromethane. Both ions abstract bromine atom from this reagent. However, **2** does so more than 300 times more efficiently than **1**. Though **2** reacts much more efficiently in this particular case, it is not uniformly more reactive than **1**. In fact, in many cases, **2** is much less reactive than **1**. For example, **1** abstracts a hydrogen atom from tetrahydrofuran with an efficiency five times greater than that of **2** and a methylthio radical from dimethyl disulfide with an efficiency six times greater than that of **2**. Further, **1** abstracts a hydrogen atom from toluene and a cyano radical from *tert*-butylisocyanide, a result also observed for the phenyl radical itself.,[16,17d] Yet neither reaction occurs with a measurable efficiency for **2** (i.e., ≥ 0.000 01). From these results, it can be

TABLE 1: Reactions of the *N*-(3-dehydrophenyl)pyridinium (1) and 3 Dehydrobenzoate (2) Ions

neutral reagent	reaction[a]	reaction efficiency[b] (1)	reaction efficiency[b] (2)	ratio of reaction efficiencies (1:2)
Tetrahydrofuran	Hydrogen abstraction	0.01	0.002	5.0
Acetone	Hydrogen abstraction	0.00004	0.00003	1.3
Toluene	Hydrogen abstraction (15%) and addition[c] (85%)	0.01	no reaction	∞
tert-Butylisocyanide	cyano radical abstraction	0.2	[d]	∞
Dimethyl disulfide	Methylthio radical abstraction	0.03	0.005	6.0
1,4-Dioxane	Hydrogen abstraction	0.05	0.01	5.0
Allyl iodide	Iodine abstraction[e]	0.1	0.023	5.0
Iodine	Iodine abstraction	0.2	1.0	0.20
Bromine	Bromine abstraction	0.05	1.0	0.050
CBr_4	Bromine abstraction	0.004	0.28	0.013
CBr_2Cl_2	Bromine abstraction	0.002	0.17	0.010
$CBrCl_3$	Bromine abstraction	0.0007	0.21	0.0035
$CHBr_3$	Bromine abstraction	0.006	0.12	0.060
	Hydrogen abstraction	0.0004	0.037	0.010

[a] The only observed reaction unless noted otherwise. [b] Reaction efficiency is defined as the ratio of the measured second-order reaction rate constant to thetheoretical collision rate constant. [c] Only 18% of this product spontaneously eliminates a hydrogen atom. [d] Slow H abstraction is observed for **2**. Only the CN abstraction is considered in the tabulated efficiencies. [e] Another minor product (10 and 22%, for **1** and **2** respectively) was also observed for both ions. This product is the *N*-(3-allylphenyl)pyridinium ion (i.e., the result of net- allyl abstraction) for **1** and iodide anion for **2**. Both of these two minor products can be rationalized by addition and subsequent elimination of iodine atom or anion, respectively. The reaction efficiencies shown above include only iodine atom abstraction pathway, which was observed for both ions.

seen that neither distonic ion is more reactive than the other in general, but that either can be much more reactive in specific cases. The variations in reaction efficiencies between **1** and **2** are significantly greater than those observed previously for distonic phenyl radical analogues with different positively charged moieties, that represent small variations in the relative distances and orientations of charged and radical moieties.[4c] It thus appears that the nature of the reaction efficiency variations must be largely attributed to the polarity of the charged moieties of the distonic ions **1** and **2**.

Discussion

The results presented in Table 1 demonstrate that the presence of the charged moiety in the distonic ions **1** and **2** has a perturbing effect on the reactivity of the phenyl radical moiety. The polarity of the charge site further appears to be important in determining the nature of this perturbation. The possible contributions of various factors to the overall perturbation are discussed in the following sections.

1. Collisional Encounter Probability. The reactivities that have been reported previously for the two distonic phenyl radical analogues **1**[4c−d] and **2**[7] are qualitatively similar to those that have been reported for the phenyl radical itself.[17] However, the reaction rate constants of the distonic analogues tend to be orders of magnitude greater than those of the neutral phenyl radical in the gas phase. The collisional encounter rates between distonic ions and neutral molecules in high vacuum are governed by long-range electrostatic attraction that dramatically increases the probability of collisions relative to collisions between the neutral phenyl radical and neutral molecules. The collision rate constant is a sensitive function of temperature, the masses of the collision partners, and the dipole moment and polarizability of the neutral molecule.[18] Small changes in any of these variables can have significant effects on the collision rate constant that will be reflected in the overall rate constant of the reaction. It is thus more meaningful from a chemical reactivity perspective to tabulate the rate constants of the ion−molecule reactions as efficiencies of reaction (i.e., the ratio of the second-order reaction rate constant to the collision rate constant) to factor out collision dynamics effects on the reaction rate.

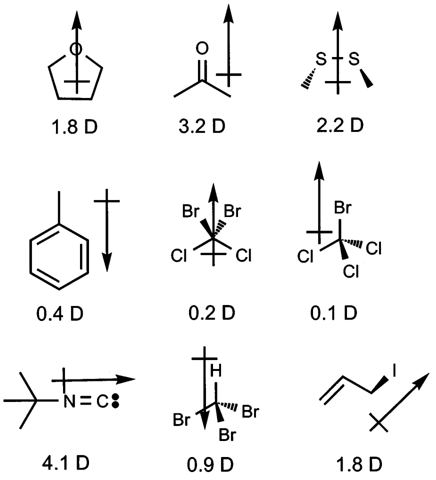
Although the collision rate constants have a great deal of influence on the overall rate of reaction for each distonic ion in the gas phase, this effect is fairly predictable. It is important to note that the long-range electrostatic interactions (i.e., ion−dipole and ion-induced dipole interactions) that control the ion−molecule collision rate in the gas phase are independent of the polarity of the ion.[18] Therefore, no bias is to be expected due to the differing charge of the two distonic ions. In fact, the only significant difference between the two ions that is relevant to the determination of the collision rate is the mass-to-charge ratio of each ion. An increase in ion mass increases the moment of inertia of ion−molecule collision pairs, and by extension, the centrifugal force that must be overcome by electrostatic attraction for a collision to occur. The simple relationship between mass and collision rate was first derived by Langevin et al.[19] in 1905 and has remained a central facet of the many derivative ion−molecule collision theories based on Langevin theory, culminating at the parametrized trajectory theory of Chesnavich et al.[10] This latter theoretical method was used here to estimate the collision rate constants necessary to convert the measured second-order reaction rate constants to reaction efficiencies. All reactivity comparisons between **1** and **2** depend for their accuracy on the correct assignment of the relative collision rates of the two distonic ions with a given neutral reagent. Any systematic error in the collision rate determination that is applied equally to both distonic ions will not impact their relative reaction efficiencies and will not impact the conclusions drawn from these relative efficiencies. The conversion to reaction efficiencies, thus, effectively factors out any systematic bias in the estimated collision rates of the two ions.

2. Ion−Molecule Solvation Effects. Even when variations in the collision rates are factored out, the presence of a distonic ion's charge will tend to increase its efficiency of reaction in high vacuum relative to neutral radicals under the same conditions. Unlike neutral radical reactions that possess a flat potential energy surface except in the region of the chemical barrier, the gas-phase potential energy surfaces for distonic ions are perturbed by the same forces of electrostatic attraction that influence the collision rate. As a molecule approaches the distonic ion, the potential energy of the ion−molecule collision complex drops significantly, reaching a minimum upon the direct interaction (H-bonding, etc.) of the charge site with the reagent molecule. Typically, ion−molecule reactions occur at these lowest-energy regions of the potential energy surface in which the neutral reagent interacts with the charge-bearing moiety. However, because the charged moieties of **1** and **2** are chemically inert toward all reagents examined in this study, reactions occur instead at the radical moiety, in a region of the potential energy surface where direct interaction between the neutral reagent and distonic ion's charged moiety is not possible. Yet, this lack of direct interaction with the charged moiety in the transition state region does not mean that it cannot affect the reaction. The transition state is lowered in energy (relative to separated reactants) by electrostatic interactions between the charged moiety and the neutral reagent. In essence, the presence of the neutral reagent serves as a source of polarizable electron density. The lowered energy of the transition state increases the rate of the reaction in a way that is directly attributable to the charged moiety.

Despite this fairly large perturbation of the reaction profile due to the presence of the charged moiety, the effects of this perturbation are fairly constant for **1** and **2**. The rigid phenyl rings of both distonic ions hold the charge and radical moieties at a constant distance and orientation, such that, the gradients of electrostatic potential emanating from the charge sites are reasonably constant. Further, in the all-important region of the radical moiety (i.e., where the chemical reaction occurs), the effect of the charge site is independent of its chemical identity. Instead, when a neutral reagent is near the radical site, it is influenced only by long-range electrostatic potentials, and the effects of the charge site can be reduced to those of a point charge of the same polarity and relative orientation with respect to the radical site. From this simplified perspective, the nature of the transition state regions[20] of both distonic ions can be seen to differ only by the polarity of the point charge that perturbs the reactivity. These two ions thus provide an ideal test of the effects of charge site polarity on the chemical reactivity of distonic ions.

As described above, the two distonic ions **1** and **2** possess quite similar relative orientations of their charged and radical moieties, with the net effect that neutral molecules in the region of the radical site experience similar degrees of ion−dipole and ion-induced dipole solvation interactions. The ion-induced dipole interaction is independent of the charge polarity. Likewise, the magnitude of the ion−dipole interaction is independent of polarity. However, the optimal orientation of polar molecules with respect to the charge site will be exactly reversed. A polar neutral molecule involved in a collision complex with one of the distonic ions will exhibit a strong tendency toward an orientation that places its molecular dipole in alignment with the charge site (i.e., with its negative pole toward a positive charge site and its positive pole toward a negative charge site). This orientation effect becomes most important if the dipole moment is large and the reaction at the radical moiety involves a transition state in which the molecular dipole is oriented toward or away from the charge site. The importance of this dipole-orientation effect undoubtedly varies considerably between the various neutral reagents examined in this work. However, it can be ruled out for the four reagents in Table 1 that do not possess a molecular dipole (i.e., iodine, bromine, 1,4-dioxane, and carbon tetrabromide). Dipole-orientation effects are further unsatisfactory explanations of the observed reactivity of **1** and **2** with two other reagents (toluene and bromotrichloromethane) whose preferred dipole orientation (calculated at the B3LYP/6-31+G(d) level of theory, Scheme 2) would suggest exactly the opposite of the observed selectivity. On the other hand, the molecular dipoles of three reagents (allyl iodide, *tert*-butylisocyanide, and dimethyl disulfide) appear to be consistent with the selectivity observed for **1** and **2**. Yet other cases are intermediate between these extremes. For example, though tetrahydrofuran possesses a strong molecular dipole, this dipole would be expected to be oriented fairly neutraly with respect to the distonic ion's charge site in a hydrogen-abstraction transition state. Others (dibromodichloromethane, bromoform, and acetone) possess sufficient rotational freedom that many possible orientations of the molecular dipole could allow reaction to occur. It thus appears clear that, although dipole orientation effects may play a role in some of these reactions, they are certainly not the only factor responsible for the observed selectivity and are probably a minor contribution to the collective selectivity in most cases.

SCHEME 2



3. Reaction Exothermicity. Beyond the perturbation arising from electrostatic stabilization of the transition state region, the intrinsic chemical reactivity of the phenyl radical moiety may be expected to be perturbed by the presence of the charge site. Any substituent might have some effect on the thermochemistry and kinetics of the reaction of a radical species. A charged substituent is merely more dramatic in its effects. A positively charged moiety can be seen as the extreme of an electron-withdrawing substituent, and likewise, a negatively charged substituent can be seen as the extreme of an electron-donating substituent. We might imagine, for example, that the electron withdrawal from and donation to the phenyl radical moiety in **1** and **2**, respectively, will cause perturbations in the overall thermochemistry of their reactions.

All the reactions reported here are calculated to be exothermic for both **1** and **2**, some by more than 30 kcal/mol (Table 2). Yet, there are systematic differences between the calculated exothermicities for the two ions. All the reactions in Table 2 correspond to either atom or group abstractions and the exothermicities of these reactions can be seen as the difference in bond dissociation energy (BDE) between the bond that is broken and the bond that is formed. Certainly, the same bond (i.e., the C−X bond of the neutral reagent) is broken in the reaction of both **1** and **2**, but a different bond is formed (i.e., the Ph-X bond of the ionic product). To the extent that the product BDE's are subject to substituent effects, there will be a trend in the exothermicities of a given type of atom abstraction. For example, all hydrogen atom abstractions are calculated to be ~5 kcal/mol more favorable for **1** (Table 2). This difference

TABLE 2: Comparison of Reaction Efficiencies and ΔH_{rxn} for Radicals 1 and 2. ΔH_{rxn} Values for the Phenyl Radical Are Provided for Comparison

neutral reagent	reaction efficiency[a] (1)	ΔH_{rxn}[b] (1) (kcal/mol)	reaction efficiency[a] (2)	ΔH_{rxn}[b] (2) (kcal/mol)	ΔH_{rxn}[b] ($Ph^{\bullet}$) (kcal/mol)
Tetrahydrofuran	0.01	−30	0.002	−26	−29
Acetone	0.00004	−10	0.00003	−5	−8
Toluene	0.01[c]	−25	no reaction	−20	−23
tert-Butylisocyanide	0.2	−32	no reaction	−44	−38
Dimethyl disulfide	0.03	−32	0.005	−28	−29
1,4-Dioxane	0.05	−27	0.01	−22	−25
Allyl iodide	0.1[d]	−24[e]	0.023[d]	−27[e]	−25[e]
Iodine	0.2	−21[e]	1.0	−25[e]	−22[e]
Bromine	0.05	−35	1.0	−38	−35
CBr_4	0.004	−27	0.28	−30	−27
CBr_2Cl_2	0.002	−35	0.17	−38	−35
$CBrCl_3$	0.0007	−32	0.21	−36	−33
$CHBr_3$	0.006[f]	−23	0.12[f]	−27	−23
	0.0004[c]	−21	0.037[c]	−16	−19

[a] Reaction efficiency is defined as the ratio of the measured second-order rate constant to the theoretical collision rate constant. [b] Calculated at the B3LYP/6-31+G(d) + ZPVE level of theory. [c] Efficiency for hydrogen atom abstraction only. [d] Efficiency for iodine atom abstraction only. [e] Calculated at the B3LYP/3-21G(d) + ZPVE level of theory. [f] Efficiency for bromine atom abstraction only.

in exothermicity for hydrogen abstraction is consistent with studies by Wenthold et al. that found that the presence of the radical site in **2** had a stabilizing effect on the anionic charge site and decreased its basicity relative to the benzoate anion.[13] Conversely, all bromine atom abstractions are calculated to be ∼4 kcal/mol more exothermic for **2** (Table 2), in qualitative agreement with the stabilizing orientation of the C−Br bond dipole in the 3-bromobenzoate product ion. Not surprisingly, the exothermicity calculated for the phenyl radical itself is usually somewhere between those of **1** and **2** in each case.

For most of the reactions shown in Table 2, the distonic ion whose reaction is more exothermic also happens to react with higher efficiency. Yet, reactivity predictions based on exothermicity fail in several important instances. For example, the two iodine donors shown in Table 2, allyl iodide and molecular iodine, show opposite trends in their reaction efficiencies, despite both reactions being calculated to be slightly (∼4 kcal/mol) more exothermic for **2**. Molecular iodine reacts five times more efficiently with **2**, but allyl iodide reacts four times more efficiently with **1**. Even more dramatically, hydrogen abstraction from bromoform occurs ∼100 times more efficiently for **2** despite this reaction being less exothermic than for **1**. This reaction contrasts with the hydrogen abstraction reactions observed for tetrahydrofuran, acetone, and toluene, all of which favor **1** over **2**. The failure of exothermicity to reflect the relative reactivity of the two distonic ions is perhaps at its worst for their reactions with *tert*-butylisocyanide. The electron-withdrawing cyano group in the abstraction product is calculated to favor **2** over **1** by 12 kcal/mol. Yet, despite this extra thermodynamic driving force for the reaction of **2** and despite the efficient CN-abstraction observed for **1**, the CN-abstraction reaction for **2** occurs at a rate too slow to be measured under these experimental conditions. Even when exothermicity correctly predicts which of the two distonic ions will be more reactive, the degree of rate difference between **1** and **2** can vary dramatically although the difference in exothermicity between the two ions stays the same (i.e., within the subset of hydrogen abstraction reactions and that of bromine abstraction reactions), and less exothermic reactions are often more efficient.

Once the above exceptions to the predictions of reactivity are noted, only the bromine atom abstractions in Table 2 appear to have more than coincidental correlation with exothermicity. However, even in the case of bromine abstraction, it is likely that the exothermicity correlation is an artifact of our selection of neutral reagents. The bromine donors examined in this work have in common high electron affinities and high ionization energies. It will be shown below that these thermochemical characteristics strongly predispose these neutral reagents to react more readily with nucleophilic (i.e., electron rich) radicals such as **2**. The trend with exothermicity is likely to be a false correlation that merely masks the importance of such polar effects on the reaction kinetics of **1** and **2**.

It seems almost impious to suggest that exothermicity is not an important contribution to the relative reaction efficiencies of **1** and **2**, but it is an impiety with precedence. Principal component analysis of the thermochemistry and barrier heights of radical reactions by Heberger et al. found that although the exothermicity of the reaction correlated strongly with the barrier heights for nonpolar radicals, this correlation faded significantly as the radicals nucleophilic or electrophilic character increased.[21] Instead, the EA of the neutral reagents became the most important predictor of the barrier heights of nucleophilic radicals and the IE became the most important predictor for electrophilic radicals.[22]

4. Polar Effects. It has been known for a great many years that electron-rich (i.e., nucleophilic) radicals and electron-deficient (i.e., electrophilic) radicals display different trends in reaction rate toward reagents that are likewise either electron rich or poor.[23] Electrophilic radicals react more rapidly with electron-rich reagents and nucleophilic radicals react more rapidly with electron-poor reagents. The molecular ionization energy (IE) of a radical provides a benchmark of its nucleophilicity and its electron affinity (EA) is a good measure of its electrophilicity. The phenyl radical itself (IE = 9.1 eV, EA = 0.61 eV; vertical values[24]) is weakly nucleophilic, but this tendency is small enough that electron-withdrawing substituents render it electrophilic.[25] The presence of a distonic ion positive charge site has just this effect, and will strongly perturb the polar character of the phenyl radical moiety. The vertical EA of the phenyl radical moiety of **1**, for example, is increased to 4.9 eV[24] and the vertical IE to 12.8 eV,[24] by the nearby presence of the positive charge, making **1** strongly electrophilic and removing any nucleophilic tendencies of the phenyl radical moiety. The negative charge site of **2** induces the opposite effect, decreasing the vertical IE of the phenyl radical moiety to 6.0 eV[24,26] and decreasing the EA to −2.6 eV,[24,27] thus making **2** strongly nucleophilic and poorly electrophilic. It can thus be seen that, even though the charge sites of **1** and **2** do not

TABLE 3: Comparison of Reaction Efficiencies and IE−EA for Radicals 1 and 2

neutral reagent	reaction efficiency[a] (1)	IE−EA[b,c] (1) (eV)	reaction efficiency[a] (2)	IE−EA[c,d] (2) (eV)
Tetrahydrofuran	0.01	4.5	0.002	7.2[f]
Acetone	0.00004	4.8	0.00003	7.3[f]
Toluene	0.013[e]	3.9	no reaction	6.0[f]
tert-Butylisocyanide	0.20	5.6	no reaction	7.0[f]
Dimethyl disulfide	0.03	4.0	0.005	5.8
1,4-Dioxane	0.05	4.3	0.01	7.4[f]
Allyl iodide	0.10[g]	4.4	0.023[g]	5.7[f]
Iodine	0.2	4.4	1.0	3.5
Bromine	0.05	5.7	1.0	3.5
CBr_4	0.004	6.5	0.28	3.9
CBr_2Cl_2	0.002	5.5	0.17	5.1[f]
$CBrCl_3$	0.0007	5.9	0.21	5.3[f]
$CHBr_3$	0.006[h]	5.6	0.12[h]	5.4[f]
	0.0004[e]		0.037[e]	

[a] Reaction efficiency is defined as the ratio of the measured second-order rate constant to the theoretical collision rate constant. [b] The IE of the neutral reagent minus the vertical EA of **1** (4.9 eV); both values calculated at the B3LYP/6-31+G(d) level of theory. [c] The IE and EA values of the neutral reagents are from ref 33 unless otherwise noted. These experimental IE and EA values are adiabatic. Adiabatic IE's are slightly smaller than vertical IE's, and adiabatic EA's are slightly larger than vertical EA's. [d] The vertical IE of **2** at the radical site (6.0 eV) calculated at the B3LYP/6-31+G(d) level of theory minus the EA of the neutral reagent. [e] Efficiency for hydrogen atom abstraction only. [f] The EA of the neutral reagent was calculated at the B3LYP/6-31+G(d) level of theory and corresponds to a vertical EA. [g] Efficiency for iodine atom abstraction only. [h] Efficiency for bromine atom abstraction only.

participate directly in the reactions of the phenyl radical moieties, their effects on the character of these reactions are nevertheless profound.

The qualitative statement that nucleophilic radicals react more rapidly with electron-deficient reagents and electrophilic radicals react more rapidly with electron-rich reagents can be made slightly more quantitative by comparing the thermochemical values (radical moiety IE and EA) of each distonic ion with those of each neutral reagent.[28] The complementary polarity of each distonic ion/neutral reagent pair can be summed up in the difference between the IE and EA of the two parties to the reaction. Two such IE-EA combinations exist: the IE of the distonic ion minus the EA of reagent and the IE of the reagent minus the EA of the distonic ion. The former IE-EA combination is predictive of nucleophilic radical reactions while the later is predictive of electrophilic reactions. The smaller the relevant IE−EA energy difference is, the more polar the transition state and the faster the reaction.[28] Because the presence of a distonic ion's charge site serves to stabilize one of these two IE-EA combinations at the expense of the other, one will be much lower in energy than the other, and the higher energy combination can be excluded from consideration. Thus, the IE of the neutral reagent minus the EA of the distonic ion will be predictive of the reaction efficiencies of **1**, whereas the IE of the distonic ion minus the EA of the neutral reagent will be predictive of the reaction efficiencies of **2**. A comparison of the relevant IE−EA term and reaction efficiencies for the reactions of both distonic ions is shown in Table 3. In each case, the relative magnitude of the IE−EA term for **1** and **2** provides a correct qualitative prediction for which of the two distonic ions will react more efficiently with a given neutral reagent. It is worth noting, however, that the IE−EA quantity is only valid in predicting which of the two distonic ions will be favored in a particular case. It does not provide a basis for predicting the efficiencies of reaction for a single distonic ion with the neutral reagents shown in Table 3. If that were the case, the reaction of **1** with dimethyl disulfide would be assumed to be the most efficient reaction shown due to its quite small IE−EA value of 2.5 eV. Yet the methylthio abstraction from dimethyl disulfide is quite different fundamentally from the hydrogen and halogen atom abstractions that occur with most of the other reagents listed in Table 3, and intercomparison is not valid.

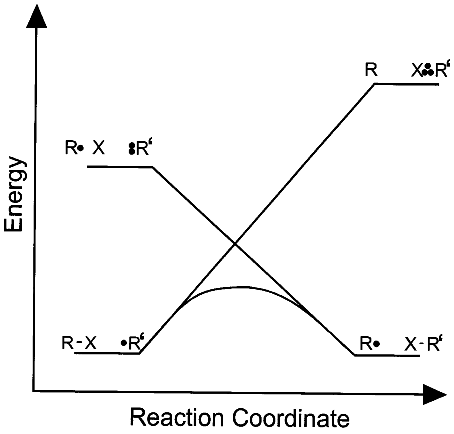


Figure 1. Example of the Anderson curve crossing diagram for the abstraction of X from R−X by radical R′.

4.1 Ionic Curve-Crossing Model. The importance of ionic states in the description of barrier formation in polar radical reactions is a key facet of the ionic curve-crossing model developed by Anderson et al. (Figure 1).[22,29] Although similar to the covalent curve-crossing model used by Shaik[30] and Pross,[31,32] the Anderson model places greater importance on ionic states than molecular singlet and triplet states. Observations of the reactions of a series of alkanes with several radicals have indicated that a stronger correlation exists between the observed reactivity and the ionic states than the analogous singlet and triplet states.[22] The ionic state is often called a "charge-transfer state" and corresponds to the transfer of an electron between the radical and reagent at every point along the reaction coordinate. The direction of the electron transfer depends on the polar character of the reactant radical. If the radical is nucleophilic, the lower-energy ionic surface (a more important contributor to the overall wave function) corresponds to electron transfer from the reactant radical to the neutral reagent. The optimal direction of electron transfer is reversed for electrophilic radicals. Thus, the energy of the ionic state relative to the reactant ground state at the reactant's geometry corresponds to the IE−EA term used in Table 3 as a barometer of polar effects. The energy of the ionic state at product geometry can similarly be estimated by the IE−EA of the products. Of course, the IE−EA values at reactant or product geometries are only first approximations of polar effects. It is the energy of the ionic state at the transition state geometry that determines its effect on the height of the reaction barrier. The energy of the ionic state at the point on the reaction coordinate corresponding to the transition state is approximated by a linear extrapolation between the reactant and product anchor points of the ionic surface.

A further insight of the Anderson model is that rigorous consideration of Coulombic stabilization of ionic states is necessary to correctly estimate the energy of ionic states. The magnitude of the stabilization can be predicted simply by $e^2/4\pi\epsilon_0 r$ (a variation of Coulomb's Law) if the distance (r) between the centers of opposite charge is known. Typical transition state *r* values are estimated from the transition state geometries and

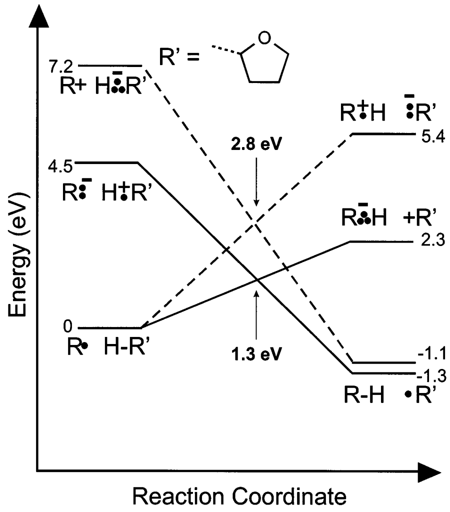


Figure 2. Anderson-type curve-crossing diagrams for the hydrogen atom abstraction by radicals **1** (solid line) and **2** (dashed line) from the 2-position in tetrahydrofuran (all energies are given in eV).

assuming that a given radical will generally undergo the same type of reaction (e.g., hydrogen atom abstraction) of a constant *r*. Thus, Coulombically stabilized ionic valence states of energy IE-EA- $e^2/4\pi\epsilon_0 r$ above product and reactant surfaces are commonly used as anchors of the ionic surfaces. Further minor corrections are also added for the polarizability of the anionic component of the ionic state, the radical's dipole moment, and the charge distribution in the ionic state. However, these later corrections have only a small effect on the overall model and can be ignored at the first level of approximation, as was done in the work described here.

So far, we have only considered the IE−EA of the reactants as a predictor of polar effects. The insight into the origin of polar effects provided by the ionic curve-crossing model suggests that, whereas this is a good first step, it is only half of the story. The remaining half is provided by consideration of the products' thermochemistry. The nature of the reactant-like ionic excited state at product geometry (i.e., the ionic excited-state anchor point at product geometry) of both **1** and **2** is controlled (as it was for the reactant excited state) by the charge site. Unlike the product-like ionic state in which the charge site influences the state energy by perturbing the thermochemistry of the phenyl radical moiety, now the charge site is attached to the nonradical species and perturbs its thermochemistry. The charge site will have a similar effect on the IE and EA of the even-electron product as it did on the reactant radical moiety. A positive charge site will raise the IE and EA of the attached moiety, and a negative charge site will lower both IE and EA of the attached moiety.

Anderson-type curve-crossing diagrams for the reactions of **1** and **2** with tetrahydrofuran are shown in Figure 2. The ground-state anchor points for the reactant and product geometries are placed at relative energies corresponding to the calculated thermochemistry of each reaction shown in Table 2. Ionic excited states are approximated by the lowest energy IE-EA combination of reactants and products. This method of estimating the ionic state energies neglects any Coulombic stabilization. This is justified by the observation that this stabilization will be less important for distonic ion systems since they correspond to ion−dipole, rather than ion−ion, interactions. Further, the similar distance of the charge site and orientation in the two distonic ions with respect to the common phenyl radical reactive moiety provide that each distonic ion will receive similar degrees of ionic state stabilization. Thus, the relative crossing point energies for the curve crossing diagrams presented for **1** and **2** provide information about the relative barrier heights of these two species without explicit consideration of this stabilization. It is important to note that even with full consideration of the Coulombic terms, the crossing points represent only an upper boundary because each reaction barrier is stabilized by the mixing of the isoenergetic valence states in the transition region leading to an avoided crossing.

The reactant sides of the curve-crossing diagram shown in Figure 2 are essentially just a graphical presentation of the IE−EA values presented in Table 3. The product sides represent complementary IE−EA values for the product radical (i.e., the tetrahydrofuran-2-yl radical) and ions (i.e., the *N*-phenylpyridinium and benzoate ions). In the case of the ionic products, the lowest-energy EA and IE represent the thermochemistry of the charged moiety rather than the C−H bond that has formed in the course of the reaction, and these thermochemical values do not provide a good estimate of the valence state that is predictive of the ionic state energy. Instead, as is often necessary with the ionic curve-crossing model, the best approximation of the ionic state corresponds to an electronic excited state, and a ΔIE or ΔEA correction is applied to the ground-state IE and EA in the amount of the energy required to promote the system to the desired excited state. Specifically, the excited-state IE and EA values used in Figures 2 − 4 correspond to the addition of an electron to the LUMO+4 molecular orbital of the *N*-phenylpyridinium cation (EA = 4.8 eV;[24] ΔEA = −0.1 eV) and removal of an electron from the HOMO-10 molecular orbital of the benzoate anion (IE = 3.9 eV;[24] ΔIE = 0.2 eV). The vertical IE and EA of the tetrahydrofuran-2-yl radical (7.0 and −1.2 eV, respectively) complete the thermochemistry needed to construct Figure 2.

The treatment of both the reactant-like and product-like ionic states (rather than merely the IE−EA of the reactants, the excited-state anchor point of the product-like state) provides important insight to the selectivity of the two distonic ions toward tetrahydrofuran. While the reactant side of the diagram only slightly favors **1** over **2**, the product thermochemistry is much more dramatically in favor of **1**. This can be easily rationalized by the observation that the tetrahydrofuran-2-yl radical is strongly nucleophilic due to stabilization of the radical site by the oxygen's lone pairs. This nucleophilic character is well matched to the electron-deficient hydrogen abstraction product of **1** (the *N*-phenylpyridinium cation) and correspondingly badly matched to the electron rich ionic product of **2**. Although hydrogen abstraction from the 2-position of tetrahydrofuran is clearly favored for **1**, **2** will likely prefer abstraction from the 3-position where the radical site is less electron-rich (EA = −0.50 eV[24]). A curve-crossing diagram for hydrogen abstraction from the 3-position by **1** and **2** is shown in Figure 3. Abstraction from the 3-position improves the outlook for **2**, but the crossing point in this case still remains higher in energy than that of **1**.

The foregoing example demonstrates how a nucleophilic radical product will favor **1** over **2**. Exactly the opposite phenomenon is observed when the product radical is strongly electrophilic. Such cases are exemplified by the bromine atom abstraction from molecular bromine (Figure 4). The radical product, bromine atom, is extremely electrophilic (IE = 11.81 eV; EA = 3.363 eV[33]), and thus more suited to the electron rich bromine-abstraction product of **2**. A quick glance at the curve-crossing diagram clearly explains why this bromine abstraction reaction proceeds at the collision rate for **2** and

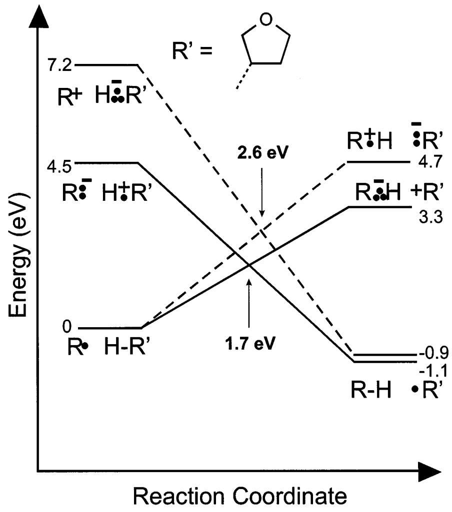


Figure 3. Anderson-type curve-crossing diagrams for the reactions of radicals **1** (solid line) and **2** (dashed line) with tetrahydrofuran by abstraction of a hydrogen atom from the 3-position. This reaction is significantly less favorable for **1** than abstraction from the 2-position (Figure 2).

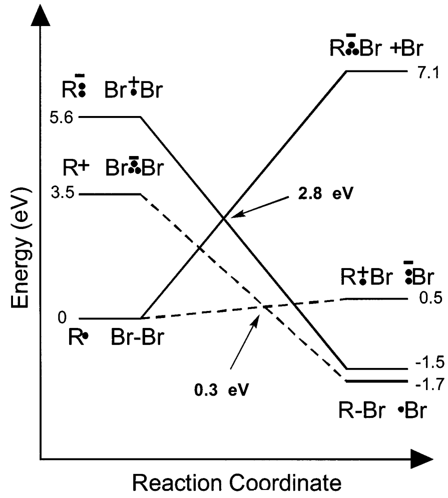


Figure 4. Anderson-type curve-crossing diagrams for the bromine atom abstraction by radicals **1** (solid line) and **2** (dashed line) from molecular bromine.

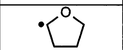
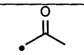
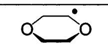
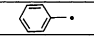
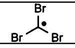
twenty-times less efficiently for **1**. The take-home message from the tetrahydrofuran and bromine examples is that the energy of the ionic excited state will be the lowest (and thus the reaction more favorable) when the product radical possesses a "philicity" that is complementary to that of the reactant distonic ion. Thus, as a general rule, electrophilic positively charged distonic ions such as **1** will be favored when the product radical is nucleophilic, and nucleophilic negatively charged distonic ions such as **2** will be favored when the product radical is electrophilic.

The insight of valence bond curve crossing models is perhaps easiest to digest in graphical form, but the essential result of relative crossing point energy can be had simply without resort to such pictorial representations via Equation 1 which relates the crossing point energy (X) (relative to the ground-state energy of the reactants) to the enthalpy of reaction (ΔH_{rxn}) and the energies of the two ionic state anchor points (I_{R} and I_{P})[22]

$$X = \frac{I_{\mathrm{R}} I_{\mathrm{P}}}{I_{\mathrm{R}} + I_{\mathrm{P}} - \Delta H_{\mathrm{rxn}}} \qquad (1)$$

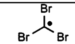
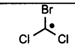
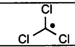
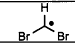
Crossing points for the hydrogen and bromine atom abstraction reactions considered here are shown in Tables 4 and 5. These values were obtained using the general approximations described above for tetrahydrofuran and Br_2 and according to eq 1. These values serve to reinforce the general polar effects predictions of Table 3.

TABLE 4: Energies of the Crossing Points in the Curve-Crossing Diagrams of the Hydrogen Abstraction Reactions of Radicals 1 and 2

Neutral Reagent	Product Radical	IE[a] (eV)	EA[a] (eV)	Crossing Point Energy[b] (1)	Crossing Point Energy[b] (2)
Tetrahydrofuran		7.0[c]	-1.2[c]	1.3	2.8
		7.9[c]	-0.5[c]	1.7	2.6
Acetone		10.0	1.4[c]	2.4	2.0
1,4-Dioxane		7.5	-0.5[c]	1.4	2.5
Toluene		7.2	0.912	1.3	1.9
Bromoform		7.5	1.7	1.6	1.4

[a] Unless otherwise noted, IE and EA values are experimental adiabatic values and were obtained from ref 33. [b] Crossing-point energies were calculated according to eq 1 with thermochemical data from Tables 2, 3, and 4. [c] Vertical value calculated at the B3LYP/6-31+G(d) level of theory.

TABLE 5: Energies of the Crossing Points in the Curve-Crossing Diagrams of the Bromine Abstraction Reactions of Radicals 1 and 2

Neutral Reagent	Product Radical	IE[a] (eV)	EA[a] (eV)	Crossing Point Energy[b] (1)	Crossing Point Energy[b] (2)
Bromine	Br•	11.8	3.4	2.8	0.3
Carbon tetrabromide		7.5	1.7	1.7	1.3
Dibromodichloromethane		8.6[c]	0.9[c]	1.9	1.6
Bromotrichloromethane		8.1	2.2	1.8	1.1
Bromoform		8.5[c]	0.7[c]	2.0	1.8

[a] Unless otherwise noted, IE and EA values are experimental adiabatic values and were obtained from ref 33. [b] Crossing-point energies were calculated according to eq 1 with thermochemical data from Tables 2, 3, and 5. [c] Vertical value calculated at the B3LYP/6-31+G(d) level of theory.

Conclusions

The main virtue of using distonic ion systems to model radical reactivity is the relative ease with which their reactivity can be studied with a wide array of powerful mass spectrometric tools and techniques. These radicals-on-a-rope can be generated in homogeneous populations, and the kinetics of even very fast reactions can be measured without confusion. Of course, the drawback of this too-good-to-be-true Faustian bargain is that the charge that provides all these benefits does so at the expense of profoundly altering the kinetics of any and all radical reactions. Because the ease of kinetic measurement is also a prime virtue of the distonic ion approach, this seems like a detriment. Yet, the reactivity of distonic ions does provide a good qualitative model of radical reactivity, and there are many circumstances where the power and flexibility of mass spectrometric experiments and the illumination they can provide outweighs the kinetic perturbation of the charge site. The kinetic influences of the ionic moiety can also often be "canceled out" by comparing the reactivity of similar distonic ion systems to assess the effects of a key remaining difference. This approach has been used successfully to study kinetic effects of substituents on reactions of N−(3-dehydrophenyl)pyridinium-type distonic ions.[34]

It is likely that the greatest contributions of the distonic ion approach to radical reaction studies will be made in the area of biradicals, triradicals, and other species[35] less amenable to convenient study in their unperturbed neutral forms. A particular strength of the use of distonic ions in the study of biradicals and related species is the ability to compare the reaction kinetics of distonic biradical ions with those of their monoradical equivalents. Such comparisons factor out most of the ionic perturbations (which are the same for both distonic monoradical and biradical ions) to directly assess the perturbation to monoradical reactivity arising from the coupling of the biradical electrons.

The overwhelming control of polar effects by the charge site of the distonic phenyl radical analogues described here emerges as an important caveat to their use as models for phenyl radical reactivity. Yet, at the same time, this sensitivity to the charge site also provides the great opportunity to study the "tuning" of polar effects by additional neutral substituents as well as by the distance, orientation, and polarity of distonic ion charge sites with respect to the radical site. In this sense, the comparison of reactions within a series of distonic ions can provide perspective into the nature of polar effects.

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(5) The symmetry of both ions places their centers of charge along the central axis of the ions. The center of charge of **1** is estimated to lie ∼0.2 Δ above the pyridinium nitrogen (still in the plane of the ring) due to delocalization of the charge within the pyridinium ring. The center of charge of **2** is estimated to lie directly between the carboxylate oxygens, ∼0.7 Δ above the carboxylate carbon.

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(26) Note that this IE of the phenyl radical moiety does not correspond to removal of an electron from the HOMO of the 3-dehydrobenzoate anion to form a biradical rather than the desired zwitterionic neutralized form. Instead, the 6.0 eV IE reflects the removal of an electron from the lower energy orbital that most closely corresponds to the SOMO of the phenyl radical.

(27) Note that this negative EA value corresponds to an ion that is unbound with respect to spontaneous electron detachment. For the purposes of polar effects, it merely serves to indicate an extreme disinclination by **2** for any electrophilic radical reactivity.

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