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# Gas-phase Reactions of the Benzyne Negative Ions

**Paul G. Wenthold,† Jun Hu and Robert R. Squires***
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

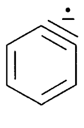
**The reactions of *o*-, *m*- and *p*-benzyne anions and the phenide ion with a series of neutral reagents are described. The *m*- and *p*-benzyne anions display similar behavior towards Brønsted acids, $CS_2$, $N_2O$, NO and $O_2$, which is analogous to that of phenide ion but clearly different from that of *o*-benzyne anion. The strongly basic and nucleophilic character of *m*- and *p*-benzyne anions dominates their reactivity, and radical-type reactions are generally not observed. Novel bifunctional reactions between *m*- and *p*-benzyne anions and both $CS_2$ and NO are observed in which two sequential S-atom abstractions and two NO additions, respectively, take place. © 1998 John Wiley & Sons, Ltd.**

KEYWORDS: benzyne; distonic ions; biradical; ion–molecule reactions; flowing afterglow

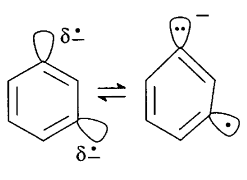
## INTRODUCTION

An important aspect of distonic ions[1] is that they can provide a means for studying free radical chemistry with a mass spectrometer. Current efforts in this area have focused on distonic ions possessing 'chemically inert' charge sites, such that the ionic reactivity is suppressed and the radical reactivity can be revealed.[2–5] Accordingly, these studies have typically involved distonic radical cations with remote, coordinatively saturated onium-type charge sites that do not possess any acidic hydrogens. Analogous investigations involving distonic radical anions with relatively unreactive charge sites have also been reported.[6–9] Valuable lessons about substituent effects on the reactivity and thermochemistry of carbon radicals are emerging from current experimental investigations of distonic ions. With distonic ions that correspond to ionized biradicals,[1] particularly those derived from biradicals in which the two coordinatively unsaturated sites are related by a molecular symmetry element, the distinction between 'ionic' and 'radical' reactivity can be somewhat obscured because the odd spin and charge density can be delocalized over both sites. This places an extra burden of proof on mechanistic assignments, since site selectivity no longer provides a distinction between the type of reaction that occurred. On the other hand, because of the presence of two potentially reactive, coordinatively unsaturated sites, ionized biradicals offer possibilities for investigating bifunctional reactivity, i.e. sequential or simultaneous reactions involving both sites. Moreover, because of the strong coupling between spin and charge at the two sites in an ionized biradical, the energetics, mechanisms and selectivities of their reactions can be different from that of 'pure' radicals or ions and, therefore, novel chemical behavior may be observed.

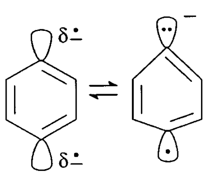
We recently described the gas-phase synthesis, identification and thermochemistry of the three isomeric benzyne anions, **1**–**3**,[10] along with a detailed theoretical analysis of their electronic structures based on an extensive series of calculations.[11] These species are prototype distonic ions of the ionized-biradical class in which the radical and charge sites are equivalent by symmetry.



**1**



**2**



**3**

The *meta* and *para* isomers were shown by the calculations to be fluxional species with low-lying, pseudo-Jahn–Teller distorted forms possessing relatively localized odd spin and negative charge density.[11] In contrast, the *ortho* isomer was found to be relatively rigid with respect to charge- and spin-localizing geometric distortions due to the weaker pseudo-Jahn–Teller interactions in this ion. The experimental results for the benzyne ions indicate a 15 kcal $mol^{-1}$ (1 kcal = 4.184 kJ) range in the heats of formation, basicities, electron binding energies and hydrogen atom affinities of the three ions, with the consistent ordering for each of these properties **1** < **2** < **3**.[10] The differing stabilities and variable electronic character of the isomeric benzyne ions offer a unique opportunity to investigate the influence of isomer energetics and charge and spin delocalization on chemical reactivity.

In this paper, we describe the gas-phase ion–molecule reactions of *o*-, *m*- and *p*-benzyne anions with a series of neutral reagents. The gas-phase reactions of *o*-benzyne anion **1** were extensively characterized previously by Guo and Grabowski.[12] These results provide useful benchmarks for evaluating the behavior of isomers **2**

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* Correspondence to: R. R. Squires, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

† Present address: Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, USA

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and **3**. Unique bifunctional ion–molecule reactions of *m*- and *p*-benzyne anions are described that distinguish them from *o*-benzyne anion, and provide new insights into the interplay between electronic structure and the 'distonic' reactivity of ionized biradicals.

## EXPERIMENTAL

All experiments were carried out at room temperature (298 ± 2 K) in a flowing afterglow triple quadrupole instrument described elsewhere.[13] Helium buffer gas was used with a total pressure, flow rate and bulk flow velocity in the flow tube of 0.4 Torr (1 Torr = 133.3 Pa) 200 STP $\mathrm{cm^3\ s^{-1}}$ and of 9700 $\mathrm{cm\ s^{-1}}$, respectively. Fluoride ion was produced in the upstream portion of the flow tube by electron impact ionization of $\mathrm{NF_3}$, and $\mathrm{OH^-}$ was produced by ionization of an $\mathrm{N_2O{-}CH_4}$ mixture. The *m*- and *p*-benzyne ions were generated by the sequence of ion–molecule reactions involving $\mathrm{F^-}$, $\mathrm{F_2}$ and the corresponding bis(trimethylsilyl)benzenes that are described in detail elsewhere.[10] *o*-Benzyne anion[12,14] was produced by reaction between benzene and $\mathrm{O^{-\bullet}}$ (formed by electron ionization of $\mathrm{N_2O}$).

Some of the ion–molecule reactions described in this study were carried out in the second quadrupole (Q2) of the triple quadrupole analyzer, which serves as a gas-tight, ion-focusing collision cell. For these experiments, the ion of interest is mass selected by the first quadrupole (Q1) and then allowed to react with a neutral reagents gas maintained in Q2 at a semi-static pressure of ∼0.08–0.30 mTorr, as indicated by an absolute pressure transducer. The kinetic energy of the reactant ion is determined by the Q2 pole offset voltage, which is kept near 0 V for examining exothermic reactions. For collision-induced dissociation (CID) experiments, collision energies of 15–20 eV (laboratory frame) were used with argon target gas pressures of 0.05–0.08 mTorr. The product ions and unreacted parent ion are extracted from Q2 with an electrostatic lens into the third quadrupole, where they are mass analyzed and then detected with an electron multiplier operated in pulse counting mode.

Kinetic measurements for ion–molecule reactions were performed by the variable-flow rate method using a pair of fixed-position ring inlets located at calibrated distances of 38 and 48 cm from the sampling orifice.[13] Neutral reagent flow rates were determined by measuring the pressure increase with time when the reagent flow is diverted from the flow tube to a calibrated volume. Absolute rate coefficients were determined with typical precision of better than ± 5% and estimated accuracy of ± 20%. Product branching ratios were determined either directly from the observed mass spectra when secondary reactions do not occur, or from the slopes of plots of the product ion yields *vs.* the extent of reactant ion conversion. For all quantitative measurements of reaction product distributions, the analyzer resolution was kept as low as possible so as to minimize ion mass discrimination. No corrections were made for differences in the diffusive loss rates for different ions. The estimated uncertainties in the product yields are ± 10%.

### Materials

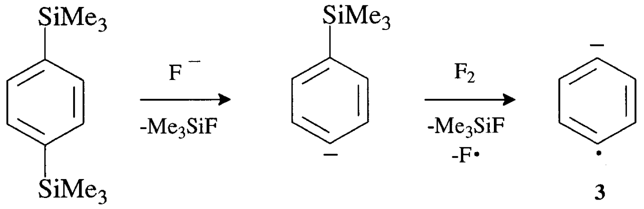
The bis(trimethylsilyl)benzenes were prepared by refluxing *m*- and *p*-dibromobenzene in tetrahydrofuran in the presence of magnesium and chlorotrimethylsilane, and were purified according to standard procedures. All other reagents were obtained from commercial sources and were used as supplied except for degassing just prior to use. Gas purities were as follows: He 99.995%, $\mathrm{F_2}$ 5% in He, $\mathrm{NF_3}$ 98%, $\mathrm{NO_2}$ 99.5%, NO 99%, $\mathrm{CO_2}$ 99.5% and $\mathrm{SO_2}$ 99.98%.

## RESULTS AND DISCUSSION

The benzyne ions **1**–**3** were generated for the ion–molecule reaction studies by well established gas-phase synthetic procedures that have been shown to produce each isomer in pure form. *o*-Benzyne anion (**1**) was produced by $\mathrm{H_2^{+\bullet}}$ abstraction from benzene by atomic oxygen anion, $\mathrm{O^{-\bullet}}$:[12,14]

$$\mathrm{O^{-\bullet}} + \mathrm{C_6H_6} \rightarrow \mathrm{H_2O} + \underset{\mathbf{1}}{o\text{-}\mathrm{C_6H_4^{-\bullet}}} \qquad (1)$$

Deuterium-labeling studies by Bruins *et al.*[14] showed that the reaction proceeds almost entirely by 1,2-abstraction to give the *ortho* radical anion isomer. *m*-Benzyne anion (**2**) and *p*-benzyne anion (**3**) were produced by the previously described[10] gas-phase synthetic sequence involving reaction of *m*- and *p*-bis(trimethylsilyl)benzene with $\mathrm{F^-}$, followed by reaction of the resulting trimethylsilylphenyl anions with molecular fluorine (Scheme 1, shown for the *para* isomer).



**Scheme 1**

This procedure produces **2** and **3** in pure form, as shown by the results of ion derivatization and authentication experiments described previously.[10]

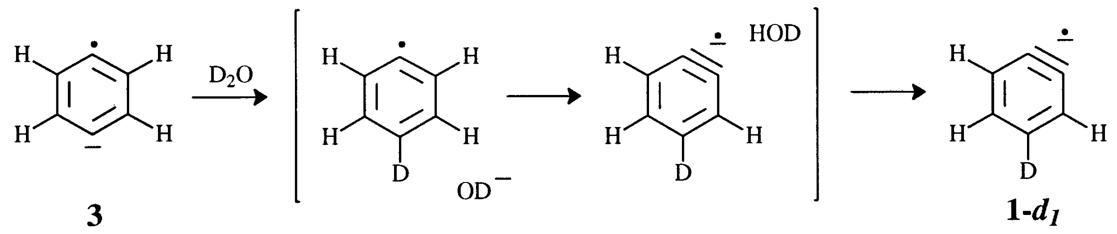
One can anticipate certain aspects of benzyne anion reactivity. Kenttämaa and co-workers[2] have demonstrated the unique bimolecular reactivity of distonic radical cations, which in some cases can be attributed to the radical site or charged site alone, but in others it appears to arise from cooperative effects of both sites. The latter processes include 'charge-catalyzed' reactions wherein the neutral reactant first interacts with the charged site, perhaps by hydrogen bonding or addition, followed by an intramolecular reaction of the coordinated reagent at the radical site. Such a mechanism requires some degree of molecular flexibility to accommodate the intramolecular reaction. Given the rigid structures of benzyne anions **2** and **3**, and relative orientations of their charge and radical sites, charge-catalyzed reactions by these isomers are unlikely. For *o*-benzyne anion **1** such mechanisms are plausible. With radical ions **2** and **3**, one may anticipate ionic reactivity characteristic of a strongly basic and nucleophilic phenyl anion and distinctive radical-type reactivity such as coupling or homolytic reactions similar to those identified for distonic phenyl radical cations.[15]

A summary listing of the products observed from the reactions of **1**–**3** and phenyl anion with a selected series of neutral reagents is given in Table 1, and a discussion of this chemistry follows. Because of the presence of other potentially reactive carbanions in the ion mixtures produced in the flow tube, most of the ion–molecule reactions described below were examined in both the flow tube and with the mass-selected $C_6H_4^{-\bullet}$ ions injected into Q2 of the triple quadrupole analyzer with minimal kinetic energies. Although ion–molecule reactions carried out in Q2 under these conditions are not necessarily thermal, the reactant ion is unambiguously determined, and the kinetic energy dependence of the product yield can provide a qualitative indication of the exo- or endothermicity of the reaction.

The acid–base chemistry and H–D exchange behavior of the benzyne anions were examined first. The proton affinity of **1** has been estimated from bracketing experiments by Guo and Grabowski[12] to be 379 ± 5 kcal $mol^{-1}$, which is in good agreement with the value of 378.2 ± 3.1 kcal $mol^{-1}$ obtained from thermochemical cycles.[10] The proton affinities of **2** and **3** were determined to be 386.9 and 393.5 kcal $mol^{-1}$, respectively, from measured heats of formation and electron affinities of the corresponding neutral species.[10] Phenide ion is a very strong base with an accurately known proton affinity of 401.7 ± 0.5 kcal $mol^{-1}$, which was derived from equilibrium proton transfer measurements[16] involving $NH_3$ ($\Delta H_{acid} = 403.6$ kcal $mol^{-1}$, Ref. 17). None of the benzyne anions appear to react with $NH_3$ in the helium flow reactor. With relatively high pressures of $ND_3$ in Q2 (0.30 mTorr) and minimal reactant ion kinetic anergies, both **2** and **3** undergo one rapid H–D exchange followed by one or two slower exchanges. Five slow H–D exchanges can be observed in the reaction between phenide ion and $ND_3$ in the flow tube, while no H–D exchange is evident with **1**.[12] Reaction between either **2** or **3** and $H_2O$ ($\Delta H_{acid} = 390.7$ kcal $mol^{-1}$, Ref. 17), in the flow tube results in partial or complete signal loss, which is attributed to precursor ion depletion effects (no $OH^-$ is observed). Ion **1** does not appear to react with $H_2O$, but it undergoes four sequential H–D exchanges with $D_2O$.[12] Reactions of **2** and **3** with $D_2O$ carried out in Q2 both result in one fast and one or two slower H–D exchanges. For ion **3**, $OD^-$ is also produced in Q2 with a collision energy dependence that indicates little or no activation energy for the reaction. We interpret the above results to mean that **2** and **3** have greater basicities than **1**, but they are easily isomerized to the more stable and less basic *ortho*- isomer by reversible proton (deuteron) transfers within the collision complexes with water or ammonia (Scheme 2, shown for **3**). This behavior precludes any attempts to determine accurate proton affinities for **2** or **3** by bracketing experiments, since the apparent 'non-occurrence' of proton transfer in a reaction with a reference acid may simply be due to isomerization to **1**. Analogous problems were encountered previously in measurements of the acidities of halobenzenes[18] and halonaphthalenes.[19]

**Table 1. Ionic products from gas-phase reactions of benzyne anions and phenyl anion with selected neutral compounds**

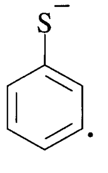
| Compound | *o*-Benzyne anion **1** | *m*-Benzyne anion **2** | *p*-Benzyne anion **3** | Phenyl anion |
|---|---|---|---|---|
| $NH_3$ | No reaction | No reaction | No reaction | $NH_2^-$ |
| $ND_3$ | No reaction | $C_6H_{4-n}D_n$ ($n = 1, 2$) | $C_6H_{4-n}D_n^{-\bullet}$ ($n = 1, 2$) | $C_6H_{5-n}D_n^{-\bullet}$ ($n = 1–5$) |
| $H_2O$ | No reaction | See text | See text | $OH^-$ |
| $D_2O$ | $C_6H_{4-n}D_n^{-\bullet}$ ($n = 1–4$) | $C_6H_{4-n}D_n^{-\bullet}$ ($n = 1, 2$) | $OD^-$, $C_6H_{4-n}D_n^{-\bullet}$ ($n = 1, 2$) | $OD^-$ |
| $CS_2$ | $CS_2^{-\bullet}$ | $C_6H_4S^{-\bullet}$, $C_6H_4S_2^{-\bullet}$ | $C_6H_4S^{-\bullet}$, $C_6H_4S_2^{-\bullet}$ | $C_6H_5S^-$, ($C_6H_5CS_2^-$) |
| $N_2O$ | No reaction | $C_6H_4O^{-\bullet}$, ($C_5H_4^{-\bullet}$) | $C_6H_4O^{-\bullet}$, ($C_5H_4^{-\bullet}$) | $C_6H_5O^-$, ($C_6H_5N_2O^-$) |
| $CH_3SSCH_3$ | $CH_3S^-$, $CH_3SCH_2S^-$ | $CH_3S^-$, $CH_3SCH_2S^-$ | $CH_3S^-$, $CH_3SCH_2S^-$ | $CH_3S^-$, $CH_3SCH_2S^-$ |
| $NO_2$ | $NO_2^-$ | $NO_2^-$ | $NO_2^-$ | $NO_2^-$ |
| NO | Signal loss | $C_6H_4NO^-$, $C_6H_4(NO)_2^{-\bullet}$ | $C_6H_4NO^-$, $C_6H_4(NO)_2^{-\bullet}$ | Signal loss |
| $O_2$ | Signal loss | $C_6H_4O^{-\bullet}$ | $C_6H_4O^{-\bullet}$, $C_5H_4^{-\bullet}$ | $C_6H_5O^-$, $C_6H_4O_2^{-\bullet}$, (c-$C_5H_5^-$) |
| RX, X = Cl, Br |  | $X^-$ | $X^-$ | $X^-$ |
| $CH_3OH$ | Signal loss | $CH_3O^-$ | $CH_3O^-$ | $CH_3O^-$ |
| $CH_3OCH_3$ |  | No reaction | No reaction | No reaction |
| $PhCH_3$ | No reaction | $PhCH_2^-$ | $PhCH_2^-$ | $PhCH_2^-$ |
| Cyclohexa-1,3-diene | c-$C_6H_7^-$ | c-$C_6H_7^-$ | c-$C_6H_7^-$ | c-$C_6H_7^-$ |

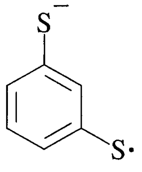


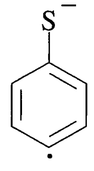
**Scheme 2**

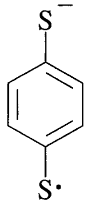
It is known that strongly basic carbanions such as vinyl or aryl ions react with $CS_2$ by sulfur atom transfer.[20] For example, phenide ion, prepared by the reaction of benzene with amide, reacts with $CS_2$ by abstraction of a sulfur atom yielding thiophenoxide ion ($C_6H_5S^-$, 95%), and by nucleophilic addition to form $C_6H_5CS_2^-$ (5%). Therefore, it is not surprising that sulfur atom transfer occurs in the reactions of **2** and **3** with $CS_2$ in the flowing afterglow. However, unlike thiophenoxide, the primary product ions from **2** and **3** (**2a** and **3a**) react further with $CS_2$ by abstraction of a second sulfur atom to produce $C_6H_4S_2^{-\bullet}$ products, which are formulated as dithiobenzoquinone radical anions, **2b** and **3b** [Eqn (2)].

$$2 \text{ or } 3 \xrightarrow[-\mathrm{CS}]{\mathrm{CS_2}} \underset{\mathbf{2a,\,3a}}{\mathrm{C_6H_4S^{-\bullet}}} \xrightarrow[-\mathrm{CS}]{\mathrm{CS_2}} \underset{\mathbf{2b,\,3b}}{\mathrm{C_6H_4S_2^{-\bullet}}} \tag{2}$$


**2a**


**2b**

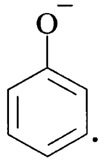

**3a**

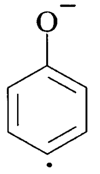

**3b**

These reactions were also carried out in Q2 of the triple quadrupole analyzer with pressures of added $CS_2$ in the range 0.01–0.10 mTorr. Under conditions of low collision energy (<0.5 eV, laboratory frame), $C_6H_4S^{-\bullet}$ and $C_6H_4S_2^{-\bullet}$ products are produced by both **2** and **3**, with $CS_2$ pressure-dependent yields that are indicative of a stepwise sulfur-abstraction mechanism. The absolute total cross-sections for reaction of both ions with $CS_2$ are estimated to be in the range 25–35 Å$^2$. The yields of **2a** and **3a** decrease sharply at higher collision energies, becoming immeasurably small at energies above 5 eV (laboratory frame). This behavior is indicative of exothermic ion–molecule reactions. Sulfur atom abstraction from $CS_2$ by phenide ion is exothermic by $\sim$18 kcal mol$^{-1}$, but for phenyl radical it is endothermic by about 8 kcal mol$^{-1}$.* Therefore, sulfur abstraction by **2a** and **3a** represents unique reactivity of the distonic species rather than pure phenyl radical reactivity. As previously reported by Guo and Grabowski,[12] and confirmed by us in the present work, *o*-benzyne anion **1** reacts with $CS_2$ exclusively by electron transfer yielding $CS_2^{-\bullet}$.† This is consistent with the known electron affinities of *o*-benzyne ($EA = 0.56 \pm 0.01$ eV[21]) and $CS_2$ ($EA = 0.895 \pm 0.020$ eV[22]). Sulfur atom abstraction by **1** is estimated to be approximately thermoneutral.†

Nitrous oxide ($N_2O$) also reacts with strongly basic carbanions in characteristic ways, producing phenoxide ions and enolate ions by oxygen atom transfer to aryl and vinyl anions, respectively.[23] Benzyne anions **2** and **3** react with $N_2O$ by oxygen atom transfer, yielding what are presumed to be the corresponding *m*- and *p*-dehydrophenoxide ions:

$$2 \text{ or } 3 \xrightarrow[-\mathrm{N_2}]{\mathrm{N_2O}} \mathrm{C_6H_4O^{-\bullet}} \xrightarrow[-\mathrm{CO}]{} \mathrm{C_5H_4^{-\bullet}} \tag{3}$$





Minor amounts (<10%) of a $C_5H_4^{-\bullet}$ ion are also produced, which is tentatively assigned the dehydrocyclopentadienide ion structure,[24] formed by decarbonylation of the dehydrophenoxides. Oxygen transfer also occurs to phenide ion along with a small amount of addition,[23] but the corresponding decarbonylation product, c-$C_5H_5^-$ is not observed. No apparent reaction takes place between $N_2O$ and **1**.[12] Kass *et al.*[23] noted the extraordinary exothermicity of oxygen transfer from $N_2O$ to phenide ion ($\Delta H = -113$ kcal mol$^{-1}$). Oxygen transfer from $N_2O$ to **1**, **2** and **3** has estimated reaction enthalpies of $-94$, $-103$ and $-109$ kcal mol$^{-1}$, respectively.‡ Decarbonylation of phenoxide ion to form cyclopentadienide ion is endothermic by $32 \pm 2$ kcal mol$^{-1}$; the energetics of this reaction with dehydrophenoxide ions should be similar. The three different behaviors exhibited by the benzyne anions and phenide with respect to decarbonylation indicate significant differences in the potential energy surfaces and/or lifetimes of the intermediates involved.

Dehydrophenoxide ions are also produced by reactions of **2** and **3** with molecular oxygen:

$$2 \text{ or } 3 \xrightarrow{\mathrm{O_2}} \mathrm{C_6H_4O^{-\bullet}}(+\ \mathrm{C_5H_4^{-\bullet}} + \mathrm{CO} \text{ for } 3) \tag{4}$$

In addition, the decarbonylation product, $C_5H_4^{-\bullet}$, is formed as a minor product by **3** (*ca.* 20%), but not by **2**. For comparison, phenide ion reacts with $O_2$ to produce $C_6H_5O^-$, c-$C_5H_5^-$ and a product ion of uncharacterized structure with *m*/*z* 108 corresponding to $[C_6H_5^- + O_2 - H]$ in approximately 5:1:5 yield ratios, respectively. The reaction between **1** and $O_2$ was reported by Guo and Grabowski[12] to proceed by associative detachment, presumably forming *o*-benzoquinone and a free electron. Oxygen transfer from $O_2$ to phenide, **1**, **2** and **3** has estimated reaction enthalpies of $-61$, $-15$, $-23$ and $-30$ kcal mol$^{-1}$, respectively.‡ Therefore, the differing reactivity of **2** and **3** with respect to decarbonylation of the intermediate dehydrophenoxides ($\Delta H \approx 32 \pm 2$ kcal mol$^{-1}$ as noted above) is probably a reflection of the thermochemistry.

Dimethyl disulfide ($CH_3SSCH_3$) has been found to be a useful reagent for probing radical reactivity of distonic

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* Estimates based on the following data (kcal mol$^{-1}$, from Ref. 17): $\Delta H_f(C_6H_5S) = 53.3 \pm 3.0$, $\Delta H_f(C_6H_5S^-) = 1.6 \pm 2.2$, $\Delta H_f(CS_2) = 28.0 \pm 0.2$, $\Delta H_f(CS) = 64.0 \pm 0.5$; $\Delta H_f(C_6H_5)$ and $\Delta H_f(C_6H_5^-)$ taken from Ref. 16.

† The presence or absence of $CS_2^{-\bullet}$ (*m*/*z* 76) as a product of reaction between $CS_2$ and **1**–**3** (also *m*/*z* 76) was determined by monitoring the signal intensity for the $^{34}$S isotopomer with *m*/*z* 78.

‡ Based on the following data taken from Ref. 17: $\Delta H_f(N_2O) = 19.6 \pm 0.1$ kcal mol$^{-1}$ $\Delta H_f(C_6H_5O^-) = -39.5 \pm 3.0$ kcal mol$^{-1}$ and an estimate for the ring C—H bond strength in phenoxide ion of 111 kcal mol$^{-1}$; $\Delta H_f$s for **1**, **2** and **3** taken from Ref. 10 are $93.7 \pm 3.1$, $102.4 \pm 3.1$ and $109.0 \pm 2.9$ kcal mol$^{-1}$, respectively.

radical cations.[25] It reacts by transfer of a methylthio group ($CH_3S$) to several different types of radical sites in distonic ions, including primary alkyl, aryl and allylic sites. However, its usefulness for characterizing distonic radical anions is limited by its manifold non-radical reactivity with many simple closed-shell anions,[26] and by the relatively high electron affinity of the methylthio radical [$EA(CH_3S) = 1.87$ eV[17]], which usually renders the methylthio group abstraction product unobservable since the resulting $CH_3S$ fragment retains the negative charge.[12,27] Dimethyl disulfide reacts with both **2** and **3** to yield $CH_3SCH_2S^-$ and $CH_3S^-$ in an approximately 1:6 yield ratio:

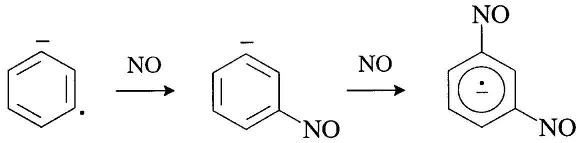
$$\begin{aligned} \mathbf{2} \text{ or } \mathbf{3} + CH_3SSCH_3 & \\ & \rightarrow CH_3SCH_2S^- + C_6H_5 \\ & \rightarrow CH_3S^- + (C_6H_5 + CH_2S) \text{ or } \\ & \qquad\qquad (C_6H_4SCH_3) \end{aligned} \quad (5)$$

The former product is observed in reactions of $CH_3SSCH_3$ with many relatively basic anions, and is believed to form by proton abstraction followed by rearrangement of the nascent $CH_3SSCH_2^-$ ion.[26] The latter product may arise either by substitution at sulfur or $\beta$-elimination. Both $CH_3SCH_2S^-$ and $CH_3S^-$ are also produced in the reaction of dimethyl disulfide with **1**[12] and with phenide ion.

The reactions of the benzyne anions with two stable free radicals were investigated. Nitrogen dioxide ($NO_2$) reacts with **1**–**3** and phenide exclusively by electron transfer, forming $NO_2^{-}$:

$$\mathbf{1, 2, 3} \text{ or } C_6H_5^- + NO_2 \rightarrow NO_2^- + C_6H_4 \text{ or } C_6H_5 \quad (6)$$

This is expected since the electron affinity of $NO_2$ (2.273 ± 0.005 eV[28]) is considerably greater than that of phenyl (1.097 ± 0.004 eV[29]) and all of benzynes [$EA$(*o*-benzyne) = 0.56 ± 0.01 eV],[21] [$EA$(*m*-benzyne) = 0.85 ± 0.01 eV],[10] [$EA$(*p*-benzyne) = 1.25 ± 0.02 eV[10]]. Nitric oxide (NO) is an open-shell molecule with an exceptionally low electron affinity [$EA(NO) = 0.026 \pm 0.005$ eV[30]]. Ions **2** and **3** both react with nitric oxide by sequential addition of two NO molecules to form dinitrosobenzene molecular anions [Eqn (7), shown for **2**].



**2** (7)

Collision-induced dissociation of the $C_6H_4(NO)_n^-$ ($n = 1, 2$) products results in exclusive loss of neutral NO molecules with collision energy thresholds for single NO loss in the 3 eV range, thereby ruling out non-covalent, cluster ion structures for these adducts. In our preliminary report on the benzyne anions,[31] we noted that *o*-benzyne anion **1** does not react with NO. This conclusion was based on the fact that neither the NO addition product nor any other organic ion products were observed when NO was added to the flow reactor, and the *assumption* that the observed decay of the *o*-benzyne anion signal was due to reaction with $NO_2$ impurity in the NO sample (since $NO_2^-$ was observed). However, new experiments with purified NO that is totally free of $NO_2$ clearly show that **1** does react away completely, but only a trace (<3% yield) of an NO-addition product is formed.* The absence of NO adduct from this reaction does not have a thermochemical basis, since deprotonation of nitrosobenzene readily occurs in the *ortho*-position to yield a stable $C_6H_4NO^-$ carbanion that exhibits a CID threshold for NO loss of >3 eV. That is, the NO binding energy of *o*-benzyne anion is comparable to that of the *meta*- and *para*-isomers.

Kinetic measurements were performed with all three benzyne ions and pure NO. The average bimolecular reaction rate coefficients obtained from replicate measurements are (4.03 ± 0.05), (2.90 ± 0.04) and (3.00 ± 0.10) × $10^{-10}$ $cm^3\ s^{-1}$ for **1**, **2** and **3**, respectively, corresponding to reaction efficiencies, $k/k_{coll}$,[32] of 0.59, 0.43 and 0.44. The NO additions to **2** and **3** need not necessarily be radical-initiated reactions, since NO also has Lewis acid character. In fact, phenide ion reacts with NO with an apparent rate coefficient, $k = (2.32 \pm 0.08) \times 10^{-10}$ $cm^3\ s^{-1}$ ($k/k_{coll} = 0.34$), that is only slightly less than those measured for the benzyne anions. This means that an unpaired electron in the reactant anion is not obligatory for reaction to occur, and that nucleophilic mechanisms can be operative. However, as with **1**, the reaction between NO and phenide ion results mainly in signal loss, and only a trace (<3% yield) of the NO-addition product is observed. Again, the virtual absence of NO adduct is not due to any thermodynamic constraints. Nitrosobenzene radical anion, $C_6H_5NO^{-\cdot}$, is a stable species with an electron binding energy of ~0.8 eV and an estimated NO dissociation energy of ~44 kcal $mol^{-1}$.†

We interpret the absence of significant yields of ionic products from the reactions of NO with **1** and phenide ion to mean that these reactions are proceeding mainly by associative detachment, i.e. the products are the corresponding neutral $C_6H_nNO$ ($n = 4, 5$) species plus a free electron:

$$\underset{\mathbf{1}}{C_6H_4} \text{ or } C_6H_5^- + NO \rightarrow C_6H_4NO \text{ or } C_6H_5NO + e^- \quad (8)$$

The above reaction is estimated to be exothermic by about 1–3 eV for phenide ion and the three benzyne anions.† Associative detachment reactions of NO with other negative ions have been reported.[34]

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* The NO reagent gas used for these kinetic measurements was purified by passage through a cold trap maintained at −78 °C interposed between the gas regulator and the flow reactor. Under these conditions, no $NO_2^-$ ions were detected, thereby confirming the removal of the $NO_2$ impurity.

† $DH[C_6H_5\text{—}NO] = 51.5 \pm 1.0$ kcal $mol^{-1}$ from Ref. 33. Combining this with $\Delta H_f(C_6H_5)$ from Ref. 16, and $\Delta H_f(NO) = 21.6$ kcal $mol^{-1}$,[17] gives $\Delta H_f(C_6H_5NO) = 51.4 \pm 1.1$ kcal $mol^{-1}$. We estimate the electron affinity of nitrosobenzene to be 18 kcal $mol^{-1}$ (slightly less than that of nitrobenzene at 23 kcal $mol^{-1}$ Ref. 17), which leads to $\Delta H_f(C_6H_5NO^{-\cdot}) = 33$ kcal $mol^{-1}$. Combining this value with $\Delta H_f(C_6H_5^-)$ from Ref. 16 gives $DH[C_6H_5^-\text{—}NO] = 44$ kcal $mol^{-1}$. Thus, the enthalpy change for Eqn (8) with $C_6H_5^-$ is approximately 18–44 = −26 kcal $mol^{-1}$. The positional acidities of nitrosobenzene are estimated to be in the range 380–388 kcal $mol^{-1}$. This leads to estimated values for $\Delta H(8)$ of −57 to −65 kcal $mol^{-1}$ for the benzyne anions.

The differing behavior with respect to product formation of **2** and **3** on the one hand and **1** and phenide ion on the other has important implications regarding the electronic structures and reaction dynamics of the isomeric benzyne anions. The *ab initio* calculations described in Ref. 11 suggest that *m* and *p*-benzyne anions are highly fluxional molecules, which exhibit low-energy 'distorted' radical anion forms with essentially localized spin and charge density at the two dehydrocarbons. In contrast, the *ortho*-isomer is calculated to be relatively rigid, and is much less susceptible to spin and charge localization through geometric distortion. The greater yields of NO-coupling products with **2** and **3** are believed to be a manifestation of their localized forms, to which radical addition can occur in a spin and symmetry-allowed manner to yield ground-state nitrosophenyl anion products that are less prone to electron detachment. Addition of NO to the closed-shell phenide ion necessarily occurs by a nucleophilic mechanism, which apparently produces metastable nitrosobenzene radical anion product states $[C_6H_5NO^{-\bullet}]^*$ that undergo electron detachment faster than collisional quenching by the helium bath gas. We can only speculate that the greater energy penalty for spin localization in ion **1** compared with **2** and **3** implied by the calculations may conduce a nucleophilic NO-addition mechanism for this isomer, which would result in the formation of excited-state *o*-nitrosophenyl anion products that rapidly detach an electron.

The reactions of ion **3** with a series of alkyl halides were investigated in order to look for halogen atom and/or alkyl group abstractions such as those reported by Kenttämaa and co-workers[15] for distonic phenyl radical cations. Among the reagents examined were methyl chloride, allyl chloride, allyl bromide, chlorodibromomethane, chlorodifluoromethane, carbon tetrachloride, α-chloro-, α-bromo- and α,α,α-trichlorotoluene and chloromethyl methyl ether ($CH_3OCH_2Cl$). However, in no case was halogen atom or alkyl group transfer observed. Rather, only the corresponding halide ions were produced as the major or exclusive ionic product, presumably by nucleophilic substitution and elimination processes. Dominance of the anion site of **3** in these reactions is consistent with its strongly basic and nucleophilic character.

Ion **3** was also allowed to react with selected molecules possessing relatively weak carbon–hydrogen bonds in order to look for hydrogen atom transfer. The reagents examined include methanol $[DH_{298}(\text{HOCH}_2\text{—H}) = 96.1 \pm 0.2\ \text{kcal mol}^{-1}]$,[35] dimethyl ether $[DH_{298}(\text{CH}_3\text{OCH}_2\text{—H}) = 93 \pm 1\ \text{kcal mol}^{-1}]$,[36] toluene $[DH_{298}(\text{PhCH}_2\text{—H}) = 89.9 \pm 0.4\ \text{kcal mol}^{-1}]$[37] and cyclohexa-1,3-diene $[DH_{298}(\text{C}_6\text{H}_7\text{—H} = 73 \pm 5\ \text{kcal mol}^{-1}]$.[36] The *para* C—H bond energy in phenide ion was determined in our earlier work[10] to be $105.4 \pm 2.9$ kcal $\text{mol}^{-1}$,[16] so hydrogen atom transfer to **3** from the reagents listed above is predicted to be exothermic by 12–32 kcal $\text{mol}^{-1}$. Although the detection of hydrogen atom transfer to the $C_6H_4^{-\bullet}$ ions is complicated by the presence of significant amounts of $C_6H_5^-$ ions in the initial mixture,[10] it is clear from the insensitivity of the $(C_6H_5^-)/(C_6H_4^-)$ ion signal ratio to changes in the concentration of added reagent that hydrogen atom transfer does not occur in any of these reactions. Proton transfer is observed from methanol $[\Delta H_{\text{acid}}(\text{CH}_3\text{OH}) = 381.5 \pm 0.1\ \text{kcal mol}^{-1}]$,[40,41] cyclohexa-1,3-diene $[\Delta H_{\text{acid}}(\text{C}_6\text{H}_8) = 373.3 \pm 4.1\ \text{kcal mol}^{-1}]$[17] and toluene $[\Delta H_{\text{acid}}(\text{PhCH}_3) = 382.3 \pm 0.3\ \text{kcal mol}^{-1}]$,[40] and **3** does not appear to react at all with dimethyl ether $[\Delta H_{\text{acid}}(\text{CH}_3\text{OCH}_3) = 407 \pm 2\ \text{kcal mol}^{-1}]$.[42] That no hydrogen abstraction occurs is unsurprising, since these types of reactions have been found to occur slowly, if at all, with many distonic radical cations.[2,43]

## CONCLUSIONS

The gas-phase reactions of the benzyne anions with a series of Brønsted acids, electrophiles and radical traps have been investigated. The *m*- and *p*-benzyne anions **2** and **3**, respectively, exhibit the same or similar reactivity towards all of the reagents examined – reactivity that differs considerably from that of the *ortho*-isomer. The greater basicities of **2** and **3** compared with **1** are evident in their reactions with acids, and the results of H–D exchange reactions indicate facile acid-catalyzed isomerization of **2** and **3** to **1**. Hydrogen- and halogen-atom abstraction reactions by the benzyne anions are not observed, but rather proton abstraction and nucleophilic processes. Ions **2** and **3** react with both $N_2O$ and $O_2$ by oxygen-atom abstraction to produce dehydrophenoxide ions, whereas **1** is unreactive with $N_2O$ and reacts by associative detachment with $O_2$. The *m*- and *p*-benzyne anions display novel bifunctional reactions with $CS_2$ and NO involving two sequential S-atom abstractions and two sequential NO additions, respectively. In contrast, *o*-benzyne anion reacts with $CS_2$ by electron transfer and with NO by associative detachment.

The negative ion chemistry of benzyne anions **1**–**3** clearly dominates their reactivity, at least for the reagents examined in this work. One approach to reducing the ionic reactivity of these species such that radical chemistry may emerge is to add Lewis acids such as $CO_2$ and $BF_3$ to the carbanion sites to produce the corresponding dehydrobenzoates[9b] and dehydrophenylborate ions,[9d] respectively. These derivatives possess far less reactive ionic sites than **1**–**3**, and represent negative ion analogs of the distonic phenyl radical cations that have been extensively characterized by Kenttämaa and co-workers.[15,40] Gas-phase radical reactivity is indeed evident with dehydrobenzoates[10,41] and dehydrophenylborate ions,[9d] although they appear to be much less reactive than analogous distonic phenyl radical cations.

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