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Reactions of the Benzyne Radical Anion in the Gas Phase, the Acidity of the Phenyl Radical, and the Heat of Formation of *o*-Benzyne

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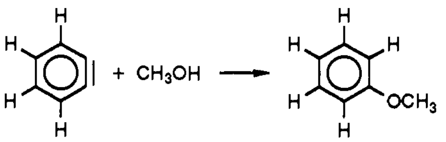
Abstract: The thermally equilibrated ion–molecule reactions of the *o*-benzyne radical anion have been examined in the gas phase with the flowing afterglow technique. By using the bracketing technique between *o*-$C_6H_4^{\bullet -}$ and Brönsted acids of known acidity, we have established the gas-phase acidity of the phenyl radical as $\Delta G^\circ_{acid}[C_6H_5^\bullet] = 371\ ^{+6}_{-3}$ kcal mol^{-1}. Combination of our experimental acidity of the phenyl radical with appropriate thermochemical data from the literature yields a variety of substantially improved thermochemical values of C_6H_4 and $C_6H_5^\bullet$ species, most notably, $\Delta H_f^\circ[o\text{-}C_6H_4] = 105$ kcal mol^{-1}. In addition to behaving as a Brönsted base, *o*-benzyne radical anion is found to undergo a number of other reactions, including electron transfer, H/D exchange, H_2^+ transfer, and direct addition. The reaction between *o*-$C_6H_4^{\bullet -}$ and the simple aliphatic alcohols is shown to be a competition between proton transfer and H_2^+ transfer while that between *o*-$C_6H_4^{\bullet -}$ and dioxygen or 1,3-butadiene is found to be exclusively an associative detachment process. One unanticipated, novel observation from these studies is the facile formation of an addition complex between the *o*-benzyne radical anion and carbon dioxide, leading to a distonic radical anion (benzoate-type anion, phenyl-type radical) that offers a unique opportunity for examining radical chemistry in ion–molecule encounter complexes.

Wittig first proposed benzyne in the early 1940s to account for the biphenyl product he isolated from the reaction of phenyllithium with fluorobenzene.[1] The first experimental proof of benzyne is often considered to be the work by Roberts and co-workers in which they showed that chlorobenzene labeled at the C-1 position with carbon-13 gave approximately a 1:1 mixture of C-1 and C-2 labeled aniline upon treatment with potassium amide/ammonia.[2] Since then, considerable experimental support has accumulated for the existence of benzyne, especially since benzyne has been generated from a variety of precursors.[3] Perhaps the most important property of benzyne is its electrophilicity as displayed by its ability to serve as a dienophile in a myriad of Diels–Alders reactions.[4] A variety of species, such as methanol[5] (eq 1) or I_2,[6] also readily add to benzyne.



(1)

In addition to mechanistic data, a variety of spectroscopic experiments have characterized benzyne. Berry and co-workers[7]

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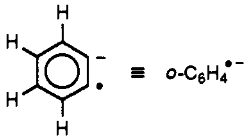
observed the UV–vis spectrum of benzyne in the vapor phase and Chapman and co-workers[8] reported the first IR spectrum[9] of benzyne in a Ar matrix at 8 K. The microwave spectrum[10] of benzyne was recently reported by Brown and co-workers while Dewar and co-workers[11] have detailed the photoelectron spectrum of benzyne.

In contrast to the considerable body of experimental work detailing the intermediacy of benzyne in a variety of reactions, there has been much less experimental work dedicated to obtaining the heat of formation of benzyne. The original report of the experimental heat of formation of *o*-benzyne by Grützmacher and Lohmann,[12] based upon studies carried out in a mass spectrometer, found $\Delta H_f°[o\text{-}C_6H_4] = 118 \pm 5$ kcal mol^{-1}. A photoelectron–photoion coincidence study by Rosenstock, Stockbauer, and Parr[13] led to a precise experimental heat of formation of $C_6H_4^+$, and that in combination with an approximate ionization potential of *o*-benzyne led these authors to estimate $\Delta H_f°[o\text{-}C_6H_4] \approx 107$ kcal mol^{-1}. In a letter, Pollack and Hehre[14] reported $\Delta H_f°[o\text{-}C_6H_4] = 118 \pm 5$ kcal mol^{-1} based upon the observation, or lack thereof, of proton transfer in the ICR from $C_6H_5^+$ to neutral bases of known proton affinity. More recently, Moini and Leroi[15] have reported a value of $\Delta H_f°[o\text{-}C_6H_4] = 100 \pm 5$ kcal mol^{-1} based upon their measurement of the appearance potential of $C_6H_4^+$ from the dibromobenzenes. Each of the reports of the heat of formation of *o*-benzyne suffers from considerable experimental uncertainties, leaving much doubt about the most accurate value for the heat of formation of *o*-benzyne.

The benzyne radical anion, $o\text{-}C_6H_4^{\bullet-}$, can be produced in the gas phase as the major ionic product from the reaction of $O^{\bullet-}$ with benzene.[16,17] The overall reaction of $O^{\bullet-}$ with benzene is extremely rapid, $k_{obs} = 2.0\ (\pm 0.2) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} (EFF = 0.96).[17] Of the reaction products that one might anticipate (eq 2) only two, $o\text{-}C_6H_4^{\bullet-}$ and $C_6H_5O^-$, have been directly observed.[17] The phenide producing channel (eq 2e) is endothermic and hence is thermochemically forbidden at 300 K. The hydride- and hydroxide-forming reactions (eqs 2c and 2d) are close to thermoneutral; that they are not an important aspect of the overall reaction of $O^{\bullet-}$ with benzene is in accord with general mechanistic perceptions (i.e., the hydride-forming channel involves addition and loss of the more basic leaving group while the hydroxide-forming channel requires an H-atom transfer, which tends not to compete well with other channels). The importance of the associative detachment channel (eq 2f) has not been accurately assessed due to the experimental difficulty of detecting detached electrons but is expected to play a minor role if any due to an unfavorable reaction pathway.[17]



$$O^{\bullet-} + C_6H_6 \xrightarrow{66\%} C_6H_4^{\bullet-} + H_2O + 9.5 \text{ kcal mol}^{-1} \quad (2a)$$

$$\xrightarrow{34\%} C_6H_5O^- + H^\bullet + 32.9 \text{ kcal mol}^{-1} \quad (2b)$$

$$\xrightarrow{0\%} H^- + C_6H_5O^\bullet - 1.0 \text{ kcal mol}^{-1} \quad (2c)$$

$$\xrightarrow{0\%} HO^- + C_6H_5^\bullet - 0.2 \text{ kcal mol}^{-1} \quad (2d)$$

$$\xrightarrow{0\%} C_6H_5^- + HO^\bullet - 18.5 \text{ kcal mol}^{-1} \quad (2e)$$

$$\xrightarrow{0\%} e^- + C_6H_5OH + 68.5 \text{ kcal mol}^{-1} \quad (2f)$$

Jennings and co-workers[16] found that the reaction of $O^{\bullet-}$ with 1,3,5-trideuteriobenzene gave predominantly HD^+-transfer, indicating that the benzyne radical anion produced is almost entirely the ortho and/or para isomers. Lineberger and co-workers[18] photodetached the benzyne radical anion which they produced by the reaction of $O^{\bullet-}$ with benzene, and from the photoelectron spectrum they deduced that $C_6H_4^{\bullet-}$ is predominantly (~98%) the ortho isomer and EA(*o*-benzyne) = 0.560 ± 0.010 eV.

An understanding of the gas-phase reactivity displayed by the benzyne radical anion would be useful for several reasons. First, by examining the facility of proton-abstraction reactions of $o\text{-}C_6H_4^{\bullet-}$ with Brönsted acids of known acidity one can determine the gas-phase acidity of the phenyl radical, an important reactive intermediate that is difficult to study directly due to its transient existence. A determination of the gas-phase acidity of the phenyl radical will lead to an accurate value of the heat of formation of *o*-benzyne. Second, $o\text{-}C_6H_4^{\bullet-}$ is a hydrocarbon radical anion, a class of ions that are relatively unstudied but whose importance and utility in solving various problems in chemistry is beginning to be recognized.[19] Third, dehydroaromatic anions such as $o\text{-}C_6H_4^{\bullet-}$ may play a useful role in the identification of mixtures of aromatic compounds by negative ion chemical ionization mass spectrometry (NICIMS)[16,17] or by atmospheric pressure ionization mass spectrometry.[20] In order to take advantage of such unique species for analytical purposes, one needs to appreciate the reactions that they may undergo under typical mass spectrometer conditions. Finally, the *o*-benzyne radical anion can, in some ways, be considered to be a carbon-based 1,2-distonic radical anion; do such species exhibit radical-type chemistry, ion-type chemistry, or some intermediate behavior? In this paper, we report our experimental observations and interpretations of the chemical reactivity displayed when $o\text{-}C_6H_4^{\bullet-}$ is allowed to react with a variety of molecules in the gas phase under the thermally equilibrated conditions uniquely attainable in a flowing afterglow. The first part of our paper resolves the uncertainty about the heat of formation of *o*-benzyne while the latter part deals with the reactivity of $o\text{-}C_6H_4^{\bullet-}$ with a variety of compounds; several of these reactions will have to be controlled in any useful analytical application of $O^{\bullet-}$ chemical ionization of aromatic compounds.

Experimental Section

The data reported in this paper have been collected by utilizing a flowing afterglow[21] that has been described previously.[22] All reactions were carried out in helium (99.99% pure and further purified by passage through a molecular sieve filled trap immersed in liquid nitrogen) buffer gas (0.3–0.7 Torr) at 298 ± 3 K, utilizing experimental methodologies that are well-documented in the literature.[21,22]

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Table I. Results from Qualitative Experiments on Gas-Phase Reactions of *o*-$C_6H_4^{\bullet-}$ with a Series of Brõnsted Acids in 0.30 Torr of Helium at 298 ± 3 K

acid	ΔG°_{acid},[a] kcal/mol	products observed	is *m/z* 76 quenched[b]
$(CH_3)_3CSH$	346.2	$(M-H)^-$	yes
c-C_5H_6	347.7	$(M-H)^-$	yes
CH_3CH_2SH	348.9	$(M-H)^-$	yes
CH_3NO_2	349.7	$(M-H)^-$	yes
CH_3SH	350.6	$(M-H)^-$; $(M-2H)^{\bullet-}$[c]	yes
CH_3CHO	359.0	$(M-H)^-$	yes
CH_3CN	365.2	$(M-H)^-$	yes
1,3-cyclohexadiene	365.9	$(M-H)^-$	yes
CH_2Cl_2	366.8	94% $(M-H)^-$; 6% $(M-2H)^{\bullet-}$[d]	yes
$(CH_3)_3COH$	368.0	$(M-H)^-$[e]	yes
CH_3CH_2OH	370.8	(see text)[e]	yes
$C_6H_5NO_2$	371	$M^{\bullet-}$	yes
$C_6H_5CH_3$	373.7	no reaction obsd	no
CH_3OH	374.0	(see text)[e]	yes
C_6H_5F	378.9	no reaction obsd	no
isoprene	379.0	no proton transfer obsd	yes[f]
furan	380	no reaction obsd[g]	no
H_2O	384.1	no reaction obsd	no
$H_2C{=}CHCH_3$	384.1	no reaction obsd[g]	no
CH_3SCH_3	386.0	no reaction obsd[g]	no
D_2O	386.1	$(o\text{-}C_6H_nD_{4-n})^{\bullet-}$, $n = 1-4$	yes
benzene	390.9	no reaction obsd[g]	no
CH_3NH_2	395.7	no reaction obsd[h]	no
NH_3	396.1	no reaction obsd[h]	no
$H_2C{=}CH_2$	397.4	no reaction obsd	no

[a] Acidities are from ref 25. Note that $(M-H)^-$ signifies the product from proton transfer, $(M-2H)^{\bullet-}$ the product from H_2^+ transfer, and $M^{\bullet-}$ the product from electron transfer. [b] "Yes" indicates that less than 1% of the initial amount of the reactant ion remains upon addition of the neutral at a port 66.6 cm from the entrance to the detection region and with a reservoir pressure of the acid of less than or equal to 2.0 Torr. [c] Only a trace amount of the $(M-2H)^{\bullet-}$ species is observed. [d] Product distribution is the average of two quantitative experiments, one of which is shown in Figure 1. [e] Chemically equivalent results were found when deuterated acid was used. [f] The only product detected is Cl^- which results from *o*-$C_6H_4^{\bullet-}$ reacting with a chlorine-containing impurity in the isoprene, i.e., no reaction occurs between the *o*-benzyne radical anion and isoprene before the benzyne radical anion is quenched by reaction with the impurity. [g] Same result is found when *o*-$C_6D_4^{\bullet-}$ is allowed to react with the neutral indicated. [h] Only *o*-$C_6D_4^{\bullet-}$ was examined with this neutral (not *o*-$C_6H_4^{\bullet-}$).

Table II. Results from Quantitative Experiments on the Rates of Gas-Phase Reactions of the Benzyne Radical Anion with Several Neutrals in Helium at 298 ± 3 K

neutral	k_{obs},[a] cm^3 $molecule^{-1}$ s^{-1}	*n*[b]	EFF[c]	P_{He} range, Torr
CH_3CN	1.81 (±0.04) × 10^{-9}	3	0.510	0.3–0.4
CH_2Cl_2	1.01 (±0.05) × 10^{-9}	4	0.631	0.3–0.4
$(CH_3)_3COH$	1.42 (±0.10) × 10^{-9}	4	0.819	0.3–0.4
CH_3CH_2OD	1.66 (±0.04) × 10^{-9}	3	0.895	0.3–0.4
CH_3OD	1.53 (±0.04) × 10^{-9}	6	0.796	0.3–0.5
$H_2C{=}CHCH{=}CH_2$	3.21 (±0.63) × 10^{-11}	10	0.0265	0.3–0.7
D_2O	3.68 (±0.27) × 10^{-10}	5	0.166	0.3–0.4
O_2	2.78 (±0.23) × 10^{-10}	9	0.448	0.3–0.7
SO_2	1.76 (±0.04) × 10^{-9}	3	1.11	0.3–0.4
CO_2	4.24 (±0.25) × 10^{-10}	10	0.560	0.3–0.4

[a] The error bars reported are one standard deviation of the population. We estimate the absolute error of these rate coefficients to be 20%; the largest contributions to absolute error are the pressure measurements (see eq 4). [b] "*n*" is the number of independent experiments used to obtain the rate coefficient listed in column 2. [c] EFF = k_{obs}/k_{coll} where k_{coll} is calculated according to the parametrized trajectory theory of Su and Chesnavich (ref 27).

Table III. Results from Qualitative Experiments on the Gas-Phase Reactions of the Benzyne Radical Anion with Several Nonacidic Neutrals in Helium at 298 ± 3 K

neutral	products obsd[a]	is *m/z* 76 quenched[b]
CS_2	$CS_2^{\bullet-}$	yes
O_2	none (see text)	yes
SO_2	$SO_2^{\bullet-}$; $(C_6H_4SO_2)^{\bullet-}$[c]	yes
$PhNO_2$	$PhNO_2^{\bullet-}$	yes
$H_2C{=}CHCH{=}CH_2$	none (see text)	yes
CO_2	$(C_6H_4CO_2)^{\bullet-}$	yes
CO	no reaction obsd	no
N_2O	no reaction obsd	no
CH_3SSCH_3	CH_3S^-; $CH_3SCH_2S^-$	yes
$CH_3OSO_2CH_3$	$CH_3OSO_2^-$	yes

[a] Except where noted, only significant products (≥10% of the overall reaction) are reported. [b] See footnote *b* of Table I. [c] By far the major product is $SO_2^{\bullet-}$ (estimated to be ca. 96% of the overall reaction at a flow tube pressure of 0.30 Torr).

The atomic oxygen anion was produced by dissociative electron attachment to nitrous oxide (eq 3) which was added, along with the helium, at the electron ionization source. Dinitrogen, at a partial pressure of 1.5

$$e^- + N_2O \rightarrow O^{\bullet-} + N_2 \qquad (3)$$

mTorr, was introduced into the flow tube 15 cm downstream of the source (107 cm from the entrance to the detection region) in order to quench any remaining metastable neutrals which may otherwise ionize the organic reagents that are added further downstream. In general, we found that for a flow tube to which only helium and nitrous oxide had been added, the amount of hydroxide (a trace impurity formed whenever we generate $O^{\bullet-}$) detected at the nose cone tended to be significantly smaller when a small amount of dinitrogen (or argon) was added as a quencher gas.

The benzyne radical anion was produced by allowing the atomic oxygen anion to react with benzene added 25 cm from the ion source (97 cm from the detection region). The molecules whose reactions with *o*-$C_6H_4^{\bullet-}$ were of interest to us were added to the flow tube at least 30 cm downstream from the point where benzene was introduced; this was the minimum distance (time) necessary to ensure that the $O^{\bullet-}$ + C_6H_6 reaction had gone to completion *before* reactions involving the molecule of interest had commenced.

All neutral reagents were obtained from standard commercial suppliers; the liquids were subjected to several freeze–pump–thaw cycles to remove dissolved gases before use. Three types of experiments were carried out in this work. All reactions reported herein were examined in a *qualitative* fashion by taking a complete mass spectrum at each of several different time points in the reaction. *Rate coefficients* were determined by monitoring the disappearance of *o*-$C_6H_4^{\bullet-}$ as a neutral reagent was added with a known constant flow rate at different distances from the entrance to the detection region (i.e., different reaction times) as previously described.[23] Equation 4 describes how the observed in-

$$k_{obs} = \frac{\Delta \ln [C_6H_4^{\bullet-}]}{\Delta(z)} \frac{F_{He}^2 T^2}{P_{He}^2 F_{molecule}} \{1.10 \times 10^{-20}\} \qquad (4)$$

tensity dependence of reaction distance yields the bimolecular rate coefficient (k_{obs} in units of cm^3 $molecule^{-1}$ s^{-1}). In eq 4, F_{He} is the volumetric flow rate of helium buffer gas (in STP cm^3 s^{-1}), P_{He} is the average flow tube pressure throughout the reaction region (in Torr), T is the ambient temperature (in K), $F_{molecule}$ is the volumetric flow rate of the neutral (in STP cm^3 s^{-1}, determined by timing a pressure rise in a calibrated volume), and z is the physical distance (in cm) between the point of molecule addition to the flow tube and the entrance to the detection region (at which point the reaction is quenched by the expansion into the high vacuum precluding further ion–molecule encounters). The constant in eq 4 contains all the necessary unit conversion parameters as well as α, which we assume to be 1.60 (i.e., the average ion velocity[24] is 1.60 times the average neutral velocity). In order to collect data at the higher flow tube pressures noted in Table II, we found it necessary to replace our 1 mm diameter sampling orifice with a 0.5 mm diameter orifice. We estimate the absolute errors on our rate coefficients as about ±20%. *Branching ratios* (i.e., relative rate coefficients, $k_i/\sum k_i$, for all primary product ion channels) were determined by monitoring reactant

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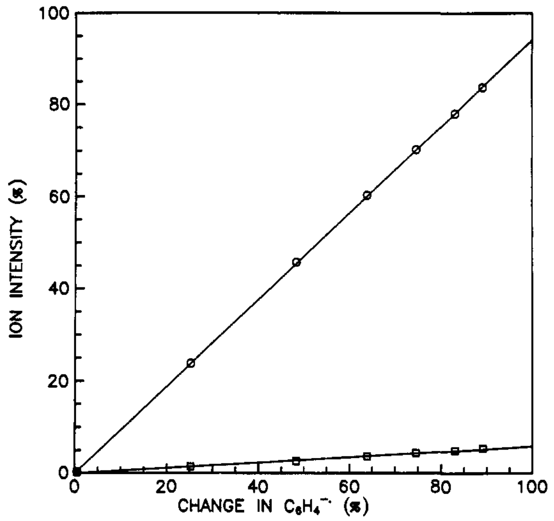

Figure 1. A plot of the relative intensities of the product ions versus the extent of reaction for the interaction of *o*-benzyne radical anion with methylene chloride. These data have been analyzed according to eq 5; the slopes of the best fit lines to the observed data points give the product distribution (relative rate coefficients) as follows: 94.1% *m/z* 83 (○), $CHCl_2^-$; 5.9% *m/z* 82 (□), $Cl_2C^{\bullet-}$.

and product ion distributions as the neutral reagent was added at different distances and then analyzing the data according to eq 5; P_i^- is a product ion, k_i is the rate coefficient for the reaction channel producing

$$[P_i^-]_t = \frac{k_i}{\sum k_i}\{[o\text{-}C_6H_4^{\bullet-}]_0 - [o\text{-}C_6H_4^{\bullet-}]_t\} \qquad (5)$$

product P_i^-, $\sum k_i$ is the total reaction rate coefficient that includes all channels, and $\{[o\text{-}C_6H_4^{\bullet-}]_0 - [o\text{-}C_6H_4^{\bullet-}]_t\}$ is the amount of the initial *o*-benzyne radical anion that has reacted. Selected examples of the data obtained for the quantitative experiments are shown below.

Results

The results of our studies on several aspects of $o\text{-}C_6H_4^{\bullet-}$ reactivity are collected in Tables I–III. In Table I, we list the qualitative results of $o\text{-}C_6H_4^{\bullet-}$ reactions with an extensive series of Brönsted acids. Column 2 lists the known gas-phase acidity of the molecule being used (in this work, we use the term "gas-phase acidity" to refer to proton loss by a neutral species and "proton affinity" (PA) to refer to proton gain by an anion), while column 3 gives a list of the product ions detected. Column 4 of Table I contains a qualitative measure of the rapidity of any reaction tried. A "yes" essentially means the rate coefficient is greater than 10^{-13} cm^3 molecule^{-1} s^{-1} while a "no" means the rate coefficient is less than this value. A quantitative measurement of the product yields for the reaction of $o\text{-}C_6H_4^{\bullet-}$ with CH_2Cl_2 was carried out and analyzed according to eq 5. One set of data is presented in Figure 1; the major ion from the reaction of $o\text{-}C_6H_4^{\bullet-}$ with H_2CCl_2 is *m/z* 83 ($HCCl_2^-$) while the minor ion is *m/z* 82 ($Cl_2C^{\bullet-}$). The observation that the data in Figure 1 are well fit by eq 5 (90% of the initial amount of $o\text{-}C_6H_4^{\bullet-}$ has undergone reaction) is an indication that there are no fast secondary reactions, in particular, $Cl_2C^{\bullet-}$ does not react with its parent compound (H_2CCl_2) by proton abstraction as do many of the carbene radical anions.[26] The lack of reaction between $Cl_2C^{\bullet-}$ and H_2CCl_2 is in accord with previous results.[22] The average of two independent branching ratio measurements for this reaction gives the results summarized in eq 6. Note that in eq 6, both the proton-transfer and the H_2^+-transfer reactions are exothermic while the H-atom transfer is endothermic (heats of reactions were determined from the data included in Table IV in the supplementary material).

$$C_6H_4^{\bullet-} + CH_2Cl_2$$

$$\xrightarrow{93.9\ (\pm 0.3)\%} HCCl_2^- + C_6H_5^{\bullet} + 6.5\ \text{kcal mol}^{-1} \qquad (6a)$$

$$\xrightarrow{6.1\ (\pm 0.3)\%} CCl_2^{\bullet-} + C_6H_6 + 29.5\ \text{kcal mol}^{-1} \qquad (6b)$$

$$\xrightarrow{0\%} C_6H_5^- + HCCl_2^{\bullet} - 7.6\ \text{kcal mol}^{-1} \qquad (6c)$$

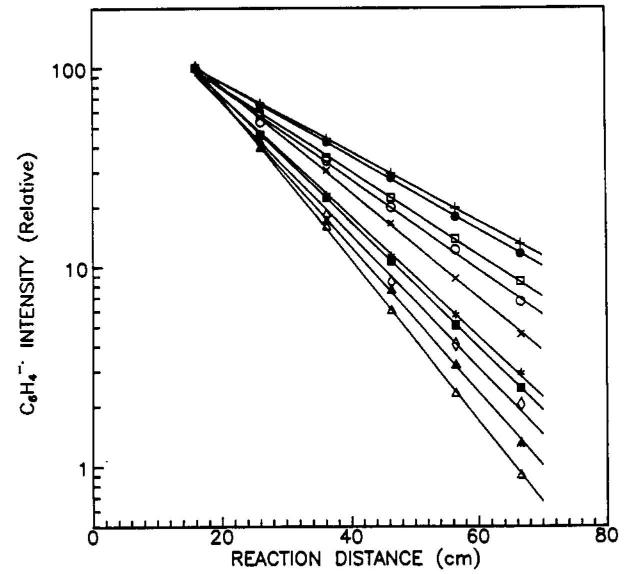

Figure 2. Representative semilogarithmic plots of reactant ion ($o\text{-}C_6H_4^{\bullet-}$) intensity versus reaction distance (time) for the series of bimolecular reactions (studied under pseudo-first-order conditions) shown in Table II. The compounds are O_2 (+, 2.9), SO_2 (●, 3.1), $H_2C{=}CHCH{=}CH_2$ (□, 3.6), CO_2 (○, 3.9), CH_2Cl_2 (×, 4.5), *t*-BuOH (*, 5.1), CH_3CN (■, 5.3), CH_3CH_2OD (◇, 5.6), D_2O (▲, 6.2), and CH_3OD (△, 6.8). This plot is representative of the type and quality of data used to arrive at the rate coefficients shown in Table II. End corrections have not been applied to these data since they would not alter the slopes from which the rate coefficients are derived. The number shown in parentheses above, following the symbol, is the number of half-lives for which this pseudo-first-order reaction was followed.

The data in Table II are the results of our quantitative studies on the rates of several $o\text{-}C_6H_4^{\bullet-}$–molecule reactions for representative proton-transfer, electron-transfer, H/D-exchange, and several other reactions. Column 4 of Table II lists the reaction efficiency which is defined as the probability of reaction per collision (EFF = k_{obs}/k_{coll}). We use the parametrized trajectory theory of Su and Chesnavich[27] to obtain the collision rate coefficients, k_{coll}. The dipole moments and polarizabilities needed to calculate the collision rate coefficients for the molecules listed in Table II are available from the literature.[28] For all the reactions listed in Table II, no pressure dependence was observed over the range of helium pressures noted in the final column. An example of one of the several independent experiments performed for each rate coefficient listed in Table II is shown in Figure 2. The number of half-lives for which the reaction of interest was followed for the experiments depicted in Figure 2 is indicated in the caption.

The results assembled in Table III are similar to those in Table I, but here we have listed the reactions for which Brönsted acid–base chemistry is not possible or is extremely unlikely. Note that the rate coefficients of a few of the reactions listed in Tables I and III are collected in Table II.

All of the heats of formations that we have referenced in this work are collected in Table IV while a partial summary of the published values of the heat of formation of *o*-benzyne is collected in Table V. Tables IV and V are included in the supplementary material.

Discussion

Proton-Transfer Reaction and the Acidity of the Phenyl Radical. As is apparent from the data in Table I, $o\text{-}C_6H_4^{\bullet-}$ will readily abstract a proton (or deuteron) from *tert*-butyl alcohol and all

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(26) McDonald, R. N. *Tetrahedron* **1989**, *13*, 3993–4015.

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

(28) *Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, 1989.

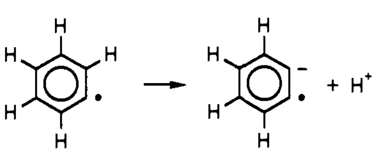
stronger acids that we have examined.[25] These observations on product ions coupled with the high efficiency displayed by the *o*-$C_6H_4^{\bullet-}$ plus $(CH_3)_3COH$ reaction (EFF = 0.82) stipulate that the phenyl radical is less acidic than *tert*-butyl alcohol, or $\Delta G^\circ_{acid}[C_6H_5^\bullet] > \Delta G^\circ_{acid}[(CH_3)_3COH] = 368.0$ kcal mol^{-1}. Methylene chloride, a carbon acid that is more acidic than *tert*-butyl alcohol, is included in the set of molecules that readily donate a proton to *o*-$C_6H_4^{\bullet-}$ (EFF = 0.63). Even acetonitrile, a carbon acid whose conjugated base is extensively delocalized, undergoes efficient acid–base chemistry with *o*-$C_6H_4^{\bullet-}$ (EFF = 0.51). Thus, the observations reported in Tables I and II firmly establish 368.0 kcal mol^{-1} as the lower limit on the acidity (ΔG°_{acid}) of the phenyl radical.

The upper limit to the acidity of the phenyl radical is more difficult to ascertain since we are unable to use $C_6H_5^\bullet$ as a proton donor to anionic bases of known proton affinity. However, we can obtain several estimates to the upper limit, the first of which we derive by an analysis of the data in Tables I and II. The reaction of *o*-$C_6H_4^{\bullet-}$ with D_2O proceeds at a rapid rate (EFF = 0.17) to give exclusively H/D exchange products. Likewise, *o*-$C_6D_4^{\bullet-}$, prepared from $O^{\bullet-}$ and perdeuteriobenzene, exchanges so rapidly and cleanly that all *o*-$C_6D_4^{\bullet-}$ can be converted to *o*-$C_6H_4^{\bullet-}$ upon reaction with H_2O. Our result, combined with the excellent understanding of base-catalyzed H/D-exchange processes in the gas phase developed by DePuy,[23,29] lets us establish that the gas-phase acidity of the phenyl radical must be at least several kilocalories per mole less than that of H_2O. This upper limit is also supported by the lack of reaction between *o*-$C_6H_4^{\bullet-}$ and propene and all weaker acids listed in Table I. Therefore, $\Delta G^\circ_{acid}[C_6H_5^\bullet] < \Delta G^\circ_{acid}[H_2O] = 384.1$ kcal mol^{-1}.

In an attempt to refine the upper limit to the acidity of the phenyl radical, we examined the reactions of *o*-$C_6H_4^{\bullet-}$ with furan, fluorobenzene, and isoprene; in neither case did we observe any proton transfer. We do not expect prohibitive kinetic barriers to exothermic proton abstraction by *o*-$C_6H_4^{\bullet-}$ from any of the Brönsted acids used since we have previously demonstrated that vinylidene radical anion abstracts protons with a discernable rate from toluene ($k_{obs} = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for $H_2C{=}C^{\bullet-}$ with $PhCH_3$, a reaction that is 4 kcal mol^{-1} exothermic).[30] Since the acidities of furan, fluorobenzene, and isoprene are not as accurately known as those used above, and since kinetic barriers to proton abstraction by *o*-$C_6H_4^{\bullet-}$ from these three acids *may* be playing a role, these data are somewhat less definitive for establishing an upper limit. A further complication for the isoprene data is the presence of a small amount of a reactive chlorine-containing impurity which will quench the benzyne radical anion signal to give Cl^-. We believe that the lack of proton transfer observed between *o*-$C_6H_4^{\bullet-}$ and furan, fluorobenzene, and isoprene is a consequence of thermochemical barriers to proton transfer, and therefore $\Delta G^\circ_{acid}[C_6H_5^\bullet] < 377.0$ kcal mol^{-1}. The lack of any reaction between *o*-$C_6H_4^{\bullet-}$ and $PhCH_3$ also supports a value of 377 kcal mol^{-1} as an upper limit.

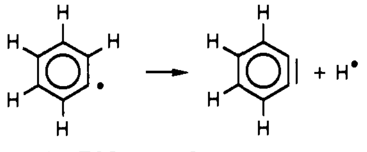
Methanol, usually an excellent molecule for bracketing studies, does undergo rapid reaction with *o*-$C_6H_4^{\bullet-}$ (EFF = 0.80), but it does not produce *any* observable ion products.[31] (We will explain below what we believe occurs for this reaction.) Since exothermic proton transfers are almost *always* observed to some extent,[32] we feel the specific observations on the methanol reaction, coupled with all other data presented here, indicate that methanol is too weak an acid to protonate *o*-$C_6H_4^{\bullet-}$. The reaction of *o*-$C_6H_4^{\bullet-}$ with ethanol, like that with methanol, proceeds predominantly by ion loss. Unlike methanol, however, where it is clear that *o*-$C_6H_4^{\bullet-}$ gives no observable product ions, it appears that ethanol gives a small amount of ethoxide along with the major "ion loss" channel. The ambiguity in the data interpretation is due to the reaction of hydroxide with ethanol to give ethoxide, coupled with the overall rapid reaction of *o*-$C_6H_4^{\bullet-}$ with ethanol. Hydroxide is a minor, but ubiquitious, impurity ion in these reactions.[17,30] As mentioned above, *o*-$C_6H_4^{\bullet-}$ reacts rapidly and cleanly with *tert*-butyl alcohol to give, as the sole product, the *tert*-butoxide ion. Our interpretation of the data for the three alcohols is as follows: $C_6H_5^\bullet$ is more acidic than methanol and less acidic than *tert*-butyl alcohol and is similar to that of ethanol. However, *o*-$C_6H_4^{\bullet-}$ is reactive with all three alcohols, with proton transfer and an alternative pathway (vide infra) in competition. To summarize then, the observations in Tables I and II allow us to establish that $\Delta G^\circ_{acid}[C_6H_5^\bullet] < 377$ kcal mol^{-1}, and they further suggest an acidity of about 371 kcal mol^{-1}.

Is the above derived acidity of the phenyl radical consistent with the facile production of *o*-$C_6H_4^{\bullet-}$ in the $O^{\bullet-}$ plus C_6H_6 reaction? To answer this question, we begin by considering the thermochemical cycle that defines the gas-phase acidity of a species in terms of a homolytic bond-dissociation energy and an electron affinity (eq 7).[33] In eq 7b, IP[$H^\bullet$] is well-known,[25] 313.6 kcal mol^{-1}, and Lineberger and co-workers[18] have an accurate value for EA[C_6H_4] = 12.9 kcal mol^{-1}. The bond-dissociation energy of the phenyl radical is available from the heats of formation as shown in eq 8. The heats of formation of the hydrogen atom and the phenyl radical are readily available,[25] 52.1 and 78.6 kcal mol^{-1}, respectively. An upper limit on the heat of formation of *o*-benzyne is available as follows. From the laboratory observation of facile *o*-$C_6H_4^{\bullet-}$ production (eq 3a), one can derive eq 9. Combining eq 9 with the definition of electron affinity leads to eq 10. Accurate



(7a)

$$\Delta H^\circ_{rxn}[\text{eq 7a}] = \Delta H^\circ_{acid}[C_6H_5^\bullet] = \text{BDE}[C_6H_4\text{–}H] - \text{EA}[o\text{-}C_6H_4] + \text{IP}[H^\bullet] \quad (7b)$$



(8a)

$$\Delta H^\circ_{rxn}[\text{eq 8a}] = \text{BDE}[C_6H_4\text{–}H] = \Delta H_f[o\text{-benzyne}] + \Delta H_f[H^\bullet] - \Delta H_f[C_6H_5^\bullet] \quad (8b)$$

$$\Delta H_{rxn}[\text{eq 2a}] = \Delta H_f^\circ[C_6H_4^{\bullet-}] + \Delta H_f^\circ[H_2O] - \Delta H_f^\circ[O^{\bullet-}] - \Delta H_f^\circ[C_6H_6] \le 0 \quad (9)$$

$$\Delta H_f[o\text{-}C_6H_4] \le \text{EA}[o\text{-}C_6H_4] - \Delta H_f^\circ[H_2O] + \Delta H_f^\circ[O^{\bullet-}] + \Delta H_f^\circ[C_6H_6] \quad (10)$$

values (Table IV)[18,25] for all the terms on the right-hand side of eq 10 lead to $\Delta H_f[o\text{-}C_6H_4] \le 116.3$ kcal mol^{-1}. Use of this limit and eq 8b leads to BDE[C_6H_4–H] ≤ 89.4 kcal mol^{-1}, and via eq 7b, $\Delta H^\circ_{acid}[C_6H_5^\bullet] < 390.1$ kcal mol^{-1}. Using $\Delta S^\circ_{acid}[C_6H_5^\bullet] = 25.7$ cal mol^{-1} K^{-1}, estimated,[33] yields $\Delta G^\circ_{acid}[C_6H_5^\bullet] \le 382$ kcal mol^{-1}. Therefore, our conclusions concerning the acidity of the phenyl radical are in accord with the observed facile production of *o*-$C_6H_4^{\bullet-}$ from $O^{\bullet-}$ with benzene.

We therefore conclude that the gas-phase acidity of the phenyl radical is definitively bracketed by $368 < \Delta G^\circ_{acid}[C_6H_5^\bullet] < 377$ kcal mol^{-1}, and furthermore, our best estimate is $\Delta G^\circ_{acid}[C_6H_5^\bullet]$

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[29] Squires, R. R.; Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 5185–5192. Grabowski, J. J.; DePuy, C. H.; Van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384–7389.

[30] Guo, Y.; Grabowski, J. J. *Int. J. Mass Spectrom. Ion Proc.* **1990**, *97*, 253–264.

[31] Traces of methoxide and the methoxide–methanol cluster ions are observed in the methanol experiment but can completely be accounted for by the reaction of the hydroxide ion impurity with methanol and the further clustering of the methoxide ion so produced. In the ethanol experiment, more ethoxide and ethoxide–ethanol cluster ions are observed than can be accounted for by the hydroxide impurity.

[32] Grabowski, J. J.; Goroff, N. Manuscript in preparation.

[33] Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11. The estimate assumes that there is no contribution to the entropy of ionization from translational, electronic, or rotational considerations while the loss of one out-of-plane sp^2 C–H bending vibration contributes −0.3 eu.

= 371 $^{+6}_{-3}$ kcal mol^{-1} and $\Delta H^\circ_{\text{acid}}[C_6H_5^\bullet]$ = 379 kcal mol^{-1}. The larger error bar on the less acidic side of our recommended value is principally due to the lack of well-defined reference acids which are not subject to possible kinetic barriers in proton-transfer reactions. Thus the phenyl radical is 21 kcal mol^{-1} more acidic than benzene. Acidities of other organic radicals and the comparison to their parent compounds have appeared in the literature previously.[26,30]

The Heat of Formation of *o*-Benzyne. Given our value for $\Delta H^\circ_{\text{acid}}[C_6H_5^\bullet]$ and eq 7b, we derive BDE[C_6H_4–H] = 78 kcal mol^{-1}. A second thermochemical definition of the gas-phase acidity of the phenyl radical is shown in eq 11. Using eq 11, our measured acidity of the phenyl radical, and the known heats of formation of H$^+$ and the phenyl radical (see Table IV), we derive ΔH_f°-

$$\Delta H^\circ_{\text{acid}}[C_6H_5^\bullet] = \Delta H_f^\circ[o\text{-}C_6H_4^{\bullet-}] + \Delta H_f^\circ[H^+] - \Delta H_f^\circ[C_6H_5^\bullet] \quad (11)$$

$[o\text{-}C_6H_4^{\bullet-}]$ = 92 kcal mol^{-1}. Using either the derived BDE-[C_6H_4–H] and eq 8b or the experimental EA[o-C_6H_4] and the definition of electron affinity with $\Delta H_f^\circ[o\text{-}C_6H_4^{\bullet-}]$ leads to ΔH_f°[*o*-benzyne] = 105 kcal mol^{-1}. Via eq 12, we can derive the

$$C_6H_5^- \rightarrow o\text{-}C_6H_4^{\bullet-} + H^\bullet \quad (12a)$$

$$\Delta H_{\text{rxn}}[\text{eq 12a}] = \text{HAA}[o\text{-}C_6H_4^{\bullet-}] = \Delta H_f^\circ[o\text{-}C_6H_4^{\bullet-}] + \Delta H_f^\circ[H^\bullet] - \Delta H_f^\circ[C_6H_5^-] \quad (12b)$$

$$C_6H_5^- \rightarrow o\text{-}C_6H_4 + H^- \quad (13a)$$

$$\Delta H_{\text{rxn}}[\text{eq 13a}] = \text{HA}[o\text{-}C_6H_4] = \Delta H_f^\circ[o\text{-}C_6H_4] + \Delta H_f^\circ[H^-] - \Delta H_f^\circ[C_6H_5^-] \quad (13b)$$

$$o\text{-}C_6H_4 \rightarrow o\text{-}C_6H_4^+ + e^- \quad (14a)$$

$$\Delta H_{\text{rxn}}[\text{eq 14a}] = \text{IP}[o\text{-}C_6H_4] = \Delta H_f^\circ[o\text{-}C_6H_4^+] + \Delta H_f^\circ[e^-] - \Delta H_f^\circ[o\text{-}C_6H_4] \quad (14b)$$

$$C_6H_5^+ \rightarrow C_6H_4 + H^+ \quad (15a)$$

$$\Delta H_{\text{rxn}}[\text{eq 15a}] = \text{PA}[o\text{-}C_6H_4] = \Delta H_f^\circ[o\text{-}C_6H_4] + \Delta H_f^\circ[H^+] - \Delta H_f^\circ[C_6H_5^+] \quad (15b)$$

H atom affinity of the *o*-benzyne radical anion as HAA[o-$C_6H_4^{\bullet-}$] = 89 kcal mol^{-1}. Via eq 13 we can derive the hydride affinity of *o*-benzyne as HA[o-C_6H_4] = 85 kcal mol^{-1}. From eq 14, which defines an ionization potential, we derive IP[o-C_6H_4] = 9.03 eV. Using our newly determined value for the heat of formation of *o*-benzyne and eq 15, we find that the proton affinity of *o*-benzyne is PA[o-C_6H_4] = 201 kcal mol^{-1}. These new values are included in Table IV.

There have been several previous experimental-based reports of the heat of formation of *o*-benzyne and numerous theoretical calculations at a wide variety of levels.[34] A sampling of the reported values are listed in Table V, which is included with the supplementary material. The reported values cluster in the 100 to 120 kcal mol^{-1} range.

Grützmacher and Lohmann[12] measured an ionization potential of *o*-benzyne and a heat of formation of $C_6H_4^+$ and from those values deduced that $\Delta H_f^\circ[o\text{-}C_6H_4]$ = 118 ± 5 kcal mol^{-1}. However, subsequent workers have suggested substantial changes to both the ionization potential[13] of $C_6H_4^+$ and the heat of formation[13,15] of $C_6H_4^+$. Thus we believe our value to be much more reliable than this early estimate.

Rosenstock and co-workers carried out a very careful photoelectron–photoion coincidence study of benzonitrile ion fragmentation as well as a thorough re-analysis of appropriate observations reported in the literature;[13] their conclusion is that $\Delta H_f^\circ[C_6H_4^+]$ = 313.3 ± 2.4 kcal mol^{-1}. Combination of this value and *a 0.5 eV empirical correction* to the published IP[o-C_6H_4] led them to estimate $\Delta H_f^\circ[C_6H_4] \approx$ 107 kcal mol^{-1}. The astonishing accuracy of this estimate for the heat of formation of *o*-benzyne is a reflection of the skill of these authors. Of particular note is that their re-interpretation of literature data led them to estimate the IP of *o*-benzyne as being identical with the value that we have derived above!

Pollack and Hehre[14] reported $\Delta H_f^\circ[o\text{-}C_6H_4]$ = 118 ± 5 kcal mol^{-1} based upon bracketing experiments in an ICR apparatus concerning the success or lack thereof of proton-transfer reactions involving $C_6H_5^+$. From their measurements, they deduced that PA(o-C_6H_4) is 9.1 kcal mol^{-1} greater than the PA of ammonia; combination of this value with the then-known heats of formation of H$^+$ and $C_6H_5^+$ led to their determination. Using the direct experimental observations reported by Pollack and Hehre and the current (slightly revised) thermochemical values[25] leads to a revised heat of formation of *o*-benzyne of 117 ± 5 kcal mol^{-1}. While we have not repeated their experiments and therefore cannot unequivocally determine why their value substantially disagrees with ours, we have pinpointed four possible complications in their experiments. First, Ausloos and co-workers[35] have demonstrated that two different populations of $C_6H_5^+$ (believed to be the phenylium ion and an open-chair isomer) can be formed in unimolecular and bimolecular ionization processes in an ICR. If the $C_6H_5^+$ ions that Pollack and Hehre were probing were in fact an unknown mixture of isomers, then the bracketed proton affinity determined is not necessarily that of *o*-benzyne. Second, Ausloos and co-workers[35] have also demonstrated that $C_6H_5^+$ ions undergo rapid, non-proton-transfer reactions with a number of molecules. Therefore, not observing proton transfer between $C_6H_5^+$ and a given molecule is not sufficient to conclude that such proton transfer is endothermic; one would wish to know that *no* reaction at all occurred (as a minimum, but not sufficient condition); such information is not provided in the Pollack and Hehre letter. Third, while many exothermic proton-transfer reactions proceed with essentially no kinetic barrier, others are known[36] to be slowed due to the presence of such barriers. The limiting bases used in the Pollack and Hehre study are some of those that one might anticipate being subject to kinetic barriers during proton-transfer reactions. Fourth, the limiting bases used in the Pollack and Hehre study themselves are not well-known; the PA of one has only been estimated. Due to these uncertainties, we feel that our value for the heat of formation of *o*-benzyne is more accurate than the value reported by Pollack and Hehre.

More recently, Moini and Leroi[15] have reported a value $\Delta H_f^\circ[o\text{-}C_6H_4]$ = 100 ± 5 kcal mol^{-1} based upon their measurement for the appearance potential of $C_6H_4^+$ from the dibromobenzenes. In their paper, they combined their directly measured value with the IP of *o*-benzyne and the heats of formation of Br$_2$ and dibromobenzene (all obtained from the literature) to derive the heat of formation of *o*-benzyne. If we combine their appearance potential with the most current values for the above mentioned thermochemical quantities,[25,37] we obtain a revised heat of formation of 104 ± 5 kcal mol^{-1}, a value that is identical for all practical purposes with our value. The agreement between Moini and Leroi's value and ours indicates that the factors (kinetic shifts, etc.) complicating determination of an adiabatic appearance energy of an ion have been correctly handled by Moini and Leroi.[15,38]

Non-Proton-Transfer Reactions of o-$C_6H_4^{\bullet-}$. The benzyne radical anion displays a number of intriguing reactions in addition to its Brönsted acid–base behavior. As mentioned above, o-$C_6H_4^{\bullet-}$ reacts rapidly with D$_2$O to give exclusively H/D exchange. Careful scrutiny of a series of qualitative spectra of this reaction,

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(34) Dewar, M. J. S.; Li, W. K. *J. Am. Chem. Soc.* **1974**, *96*, 5569–5571 and references therein.

(35) Ausloos, P.; Lias, S. G.; Buckley, T. J.; Rogers, E. E. *Int. J. Mass Spectrom. Ion Proc.* **1989**, *92*, 65–77.

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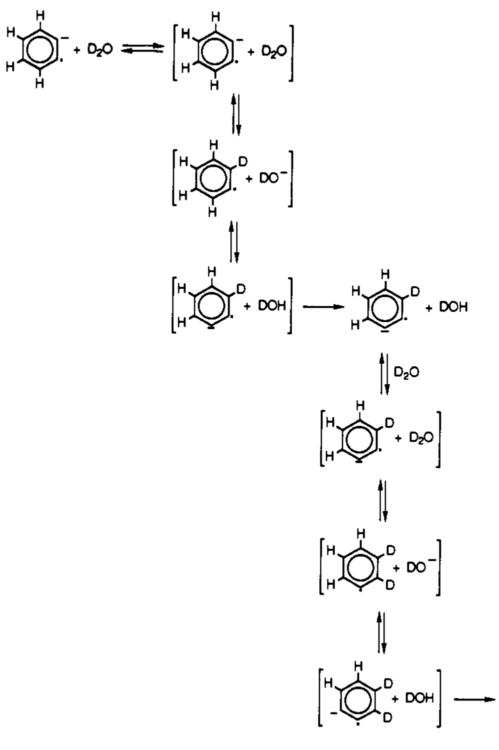
(37) Rosenstock, H. M.; Stockbauer, R.; Parr, A. C. *J. Chim. Phys.* **1980**, *77*, 745–750.

(38) Vestal, M. In *Fundamental Processes in Radiation Chemistry*; Ausloos, P., Ed.; Interscience: New York, 1968.

Scheme I. Stepwise Base-Catalyzed H/D Exchange between *o*-Benzyne Radical Anion and Water[a]



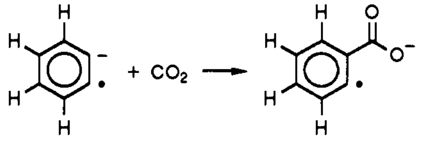
[a] The proposed intermediates, which are not observed, are shown within brackets. Note that the scheme displays two sequential exchange reactions, a discrete intermediate product ion is *o*-$C_6H_3D^{\bullet-}$.

and of *o*-$C_6D_4^{\bullet-}$ with H_2O, suggests that essentially a single D(H) is exchanged per ion–water encounter. A stepwise exchange mechanism is presented in Scheme I. We restrict ourselves to *o*-benzyne isomers in Scheme I because negative ion photoelectron spectroscopy[18] and a number of ab initio calculations[34] indicate that *o*-benzyne is the lowest energy isomer. Note that in this regard, we consider that the *o*-benzyne radical anion has two equivalent resonance structures (i.e., carbon-1 as radical/carbon-2 as anion or carbon-1 as anion/carbon-2 as radical). Neither ammonia nor methylamine was found to undergo H/D exchange (nor any reaction) with *o*-$C_6D_4^{\bullet-}$. If the acidity of the phenyl radical was in fact about 391 kcal mol^{-1} as derived from the previous experimental $\Delta H_f°$[*o*-benzyne], one should expect facile exchange between *o*-$C_6H_4^{\bullet-}$ and NH_3 or a simple alkylamine.[39] The inertness displayed by *o*-$C_6H_4^{\bullet-}$ toward NH_3 and CH_3NH_2 is further confirmation of our acidity (379 kcal mol^{-1}) of the phenyl radical. When *o*-$C_6H_4^{\bullet-}$ was allowed to react with CH_3OD, the only process observed was the same rapid reaction that removes all ions as was observed in the CH_3OH reaction. The lack of H/D exchange between the *o*-benzyne radical anion and methanol-*O*-*d* is presumably due to the competing fast reaction that results in ion signal loss.

Whenever *o*-$C_6H_4^{\bullet-}$ is allowed to react with a molecule for which electron transfer is a thermochemically accessible channel (e.g., CS_2, EA = 0.6 ± 0.1 eV; $PhNO_2$, EA = 0.97 eV; SO_2, EA = 1.107 ± 0.008 eV)[40] the predominant, if not exclusive, process observed is electron transfer. As expected from the known electron affinities of *o*-benzyne and dioxygen (EA[O_2] = 0.451 eV),[41] no electron transfer was observed when *o*-$C_6H_4^{\bullet-}$ was allowed to react with O_2, a reaction that is 2.5 kcal mol^{-1} endothermic. We have characterized the absolute rate for *o*-$C_6H_4^{\bullet-}$ interacting with SO_2 and found $k_{obs} = 1.76\ (\pm 0.04) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} or EFF = 1.11. We realize that an EFF greater than 1 is, in some ways, meaningless and therefore would like to address several comments to it. First, an absolute error bar of ±20% exists for k_{obs}; hence the EFF is within the error of 1.00. Second, the error bar on a reaction EFF also depends on how well k_{coll} is known, which is to say, the accuracy of the theory used[27] and the parameters employed (i.e., for SO_2: $\mu_D = 1.63$ D; $\alpha = 4.28 \times 10^{-24}$ cm^{-3}).[28] Third, other reports of EFF > 1 for reactions involving SO_2 where ET is the major component have appeared.[42] Finally, for this work, it is only SO_2 for which EFF exceeds 1 (also the only ET rate coefficient measured). While recognizing that we cannot make a definitive statement about why EFF > 1 for *o*-$C_6H_4^{\bullet-}$ + SO_2, we would like to suggest that it is either due to a poorly known μ_D or α value of SO_2 or, perhaps, electron transfer can occur over a larger distance than is normally assumed when defining an ion–molecule encounter. Another interesting aspect of the *o*-$C_6H_4^{\bullet-}$ plus SO_2 reaction is the observation that a minor amount (ca. 4% of the products formed) of adduct ion ($C_6H_4SO_2^{\bullet-}$) is formed in competition with the electron-transfer process.

The *o*-benzyne radical anion is nucleophilic toward both carbon and sulfur as exhibited by its reactions with dimethyl disulfide[43] and dimethyl sulfite.[44] *o*-$C_6H_4^{\bullet-}$ is unreactive toward both carbon monoxide and nitrous oxide, observations that are in agreement with previously observed reactivity patterns of these molecules.[45]

As do many anions,[46] the benzyne radical anion adds readily to CO_2 to give the adduct in a reaction that occurs on 56% of the collisions. The rate coefficient for *o*-$C_6H_4^{\bullet-}$ and CO_2 shows no pressure dependence in the 0.3–0.7 Torr (helium) range that we examined. Since the product of the *o*-$C_6H_4^{\bullet-}$ and CO_2 reaction is the addition complex, $C_7H_4O_2^{\bullet-}$, and since this adduct is unreactive toward additional equivalents of CO_2 or toward D_2O, we formulate the adduct as a distonic radical anion consisting of a phenyl radical and a carboxylate anion (eq 16). The adduct ion, $C_7H_4O_2^{\bullet-}$, does undergo both slow exchange with SO_2 (SO_2 for CO_2, eq 17a)[47] and further addition (eq 17b). These SO_2 observations indirectly support our structural assignment to the $C_7H_4O_2^{\bullet-}$ species.



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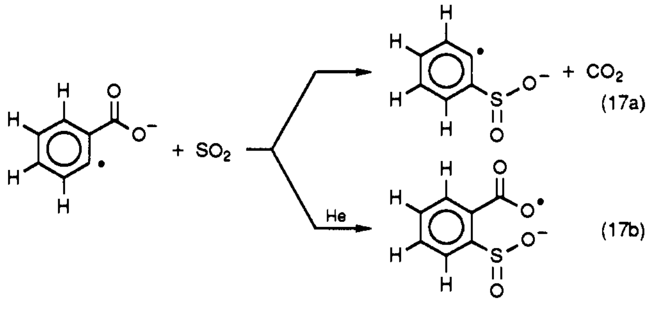

(17a)

(17b)

Another important point is answered by our qualitative studies between the *o*-benzyne radical anion and carbon dioxide and the

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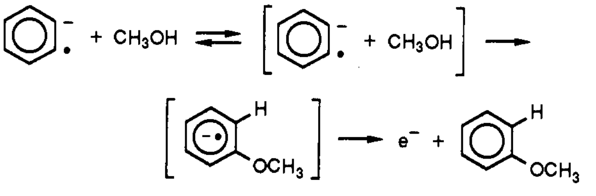
subsequent reactions of the resulting adduct. To experimentally study reaction 17, the list of events involving ions is as follows: (i) The atomic oxygen anion is created by electron ionization of nitrous oxide. (ii) The atomic oxygen anion is quenched by benzene as described in eq 2, producing 66% $C_6H_4^{\bullet-}$ and 34% $C_6H_5O^-$. (iii) Carbon dioxide is added so that the *o*-benzyne radical anion is quenched, resulting in production of the adduct ion at *m/z* 120. (iv) Sulfur dioxide is added and its chemistry with the *m/z* 120 ion is investigated.

During step iii of the above list of events, the phenoxide ion that is present remains unchanged since $C_6H_5O^-$ is unreactive toward CO_2; therefore upon quenching of the *o*-$C_6H_4^{\bullet-}$ signal, the ion spectrum contains $C_7H_4O_2^{\bullet-}$ (*m/z* 120) and $C_6H_5O^-$ (*m/z* 93). During step iv, both the *m/z* 93 and 120 ions are moderately reactive with SO_2 (*m/z* 93 produces only the corresponding adduct while *m/z* 120 reacts according to eq 17), and in fact we can easily quench both signals. Because 34% phenoxide is initially formed along with the *o*-benzyne radical anion, and because phenoxide is fairly unreactive (e.g., does not react with carbon dioxide but does react with sulfur dioxide), we used the phenoxide signal as a marker ion to indicate whether or not a radical anion reaction gave significant amounts of some sort of detachment process (as in the methanol reaction discussed below). Thus during the CO_2 reaction, the ratio of *m/z* 76 ($C_6H_4^{\bullet-}$) to *m/z* 93 ($C_6H_5O^-$) signals before reaction is the same as the ratio of the *m/z* 120 ($C_7H_4O_2^{\bullet-}$) to *m/z* 93 signals after the reaction, telling us that no associative detachment occurred between the *o*-benzyne radical anion and carbon dioxide. The same type of observations help define the quantitative nature of the associative detachment reaction that does occur between the *o*-benzyne radical anion and methanol as well as the general unimportance of such a process (excepting ethanol) for most of the other compounds examined in this study.

Reactions of $C_6H_4^{\bullet-}$ with Alcohols. We were initially puzzled by the data for the reactions of *o*-$C_6H_4^{\bullet-}$ with methanol, ethanol, or *tert*-butyl alcohol. The tertiary alcohol was observed to react rapidly with *o*-$C_6H_4^{\bullet-}$ (EFF = 0.82) to give *tert*-butoxide, which is quantitatively detected. In stark contrast, we found that *o*-$C_6H_4^{\bullet-}$ reacts rapidly with methanol (EFF = 0.80) but *could detect no product ions*! Ethanol is intermediate to *tert*-butyl alcohol and methanol; reaction with *o*-$C_6H_4^{\bullet-}$ is rapid (EFF = 0.90), and some ethoxide is formed, but there is also considerable loss in the total ion current. The presence of phenoxide and its unreactive nature toward these alcohols aid in defining these observations.

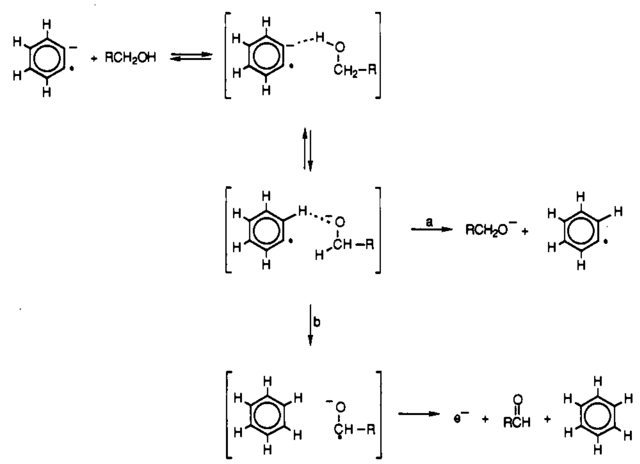
We had originally interpreted these alcohol reactions to indicate some sort of associative detachment process that produced the alkyl phenyl ether (i.e., in analogy to eq 1). For example, the original mechanistic proposal for methanol is shown in eq 18. However, such a process was not very satisfying since it involved the intermediacy of the molecular radical anion of anisole—a species that probably is not bound and therefore would autodetach—without a reasonable mechanism for it to be formed. Furthermore, the differences between the three alcohols, while explainable, do not seem to follow expectations based on eq 18.



(18)

Our unease with eq 18 to explain the alcohol data led us to reconsider the expected neutral product from the methanol reaction—a species which we cannot directly observe! We propose that the products from the reaction of *o*-$C_6H_4^{\bullet-}$ with CH_3OH are benzene plus formaldehyde and an electron. The process we prefer for the alcohols is summarized in Scheme II. For our discussion we will consider how *o*-$C_6H_4^{\bullet-}$ reacts with methanol. Initially, $C_6H_4^{\bullet-}$ collides with methanol to create the ion–dipole complex. Formally, we believe it is endoergic by 3 kcal mol^{-1} to transfer the proton from methanol to *o*-$C_6H_4^{\bullet-}$ (it is thermoneutral to transfer from ethanol and exoergic from *tert*-butyl alcohol). Since both methoxide and the benzyne radical anion may be considered to be localized anions, and due to their similar basicities, we can anticipate that a good hydrogen bond can exist in the initial complex (first bracketed species in Scheme II).[48] Depending on the exact system being studied, the more stable form of the initial ion–dipole complex may be that which results from a proton transfer (i.e., yielding the second bracketed species in Scheme II); the factors that contribute to determining whether the first intermediate or the second intermediate is more stable are the relative basicities of the anions *and* the relative solvation energies of the two complexes.[23] If net proton transfer is thermochemically feasible, the second intermediate complex can dissociate (path a) to give alkoxide ion. Alternatively, if net proton transfer is thermoneutral or slightly endothermic (as we propose for methanol) the hydrogen-bonded complex shown as the second intermediate in Scheme II will facilitate H atom abstraction as indicated by path b. H atom transfer, driven by the formation of an aromatic C–H bond (e.g., BDE[C_6H_5–H] = 110.9 ± 1.9 kcal mol^{-1})[25] at the cost of breaking an aliphatic C–H bond adjacent to oxygen (e.g., BDE[$HOCH_2$–H] = 94 ± 2 kcal mol^{-1})[49] leads to benzene and the ketyl radical anion (i.e., oxidation of the initial alcohol). Since it is believed that the molecular anion of formaldehyde (and acetaldehyde[50]) is not bound, the ketyl radical anion will autodetach leading to net ion loss. *tert*-Butoxide of course does not have the α-C–H bond demanded by our hypothesis; the clean observation of proton transfer for this latter case is in accord with path a of Scheme II. Methanol goes cleanly by path b and ethanol partitions itself through both pathways with path b being predominant. The observation of the $(M-2H)^{\bullet-}$ species from *o*-$C_6H_4^{\bullet-}$ with methanethiol (Table I) also supports Scheme II. For this latter molecule, direct proton transfer predominates over other pathways, but formation of benzene does occur as evidenced by the ketyl radical anion of thioformaldehyde, a species that we know is bound.[51] We prefer Scheme II over eq 18 to account for our observations about how *o*-$C_6H_4^{\bullet-}$ reacts with alcohols (and to a lesser extent, with thiols). The lack of *any* product ion from methanol is due to the slight endoergicity of the proton-transfer channel and the unbound nature of the formaldehyde radical anion. Ethanol is identical, in acid strength, to phenyl radical, and hence direct proton transfer is observed while the major portion of the reaction proceeds by path b in Scheme II. *tert*-Butyl alcohol is acidic enough to allow rapid, exoergic proton transfer with *o*-$C_6H_4^{\bullet-}$ and therefore the overall rate is not slowed due to the inaccessibility of the second hydrogen necessary for path a. The

Scheme II. Proposed Reaction Scheme for Primary Alcohols with the *o*-Benzyne Radical Anion



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observation of both ethoxide and ion loss for $o\text{-}C_6H_4^{\bullet -}$ + EtOH suggests that a stepwise process (as shown in Scheme II) adequately accounts for these alcohol reactions without need of resorting to a highly ordered concerted pathway.

Reaction of $C_6H_4^{\bullet -}$ with Dioxygen and Butadiene. We examined the reaction of the *o*-benzyne radical anion with both O_2 and $H_2C{=}CHCH{=}CH_2$ (data in Tables II and III). For both cases reaction is observed that completely quenches the $o\text{-}C_6H_4^{\bullet -}$ signal in a pressure-independent manner (0.3–0.7 Torr of helium). The dioxygen reaction is faster (EFF = 0.45) than the butadiene reaction (EFF = 0.027), and both reactions proceed exclusively by an associative detachment channel. Here again, the presence of the phenoxide signal serves as a marker ion to confirm the absence of any spurious ion sampling effects upon the addition of either of these molecules. Unfortunately, we have no additional information to help identify the chemical processes that are occurring in these two reactions. For dioxygen, we can speculate that the products are a free electron and *o*-benzoquinone since such a reaction is 123 kcal mol^{-1} exothermic, providing ample energy to detach any *o*-benzoquinone radical anion formed (EA-[*o*-benzoquinone] = 1.620 ± 0.048 eV).[52] For butadiene, we can speculate that the products are a free electron, benzene, and but-3-en-1-yne ($H_2C{=}CHC{\equiv}CH$) since such a reaction is 27 kcal mol^{-1} exothermic. An unsatisfying aspect of this latter explanation is if the H_2^+-transfer and subsequent electron detachment process is in fact occurring between butadiene and the *o*-benzyne radical anion, then why is a similar reaction *not* found for propene (such a process to yield a free electron, benzene, and allene should be 33 kcal mol^{-1} exothermic). An obvious alternative product for the *o*-benzyne radical anion with butadiene is the Diels–Alder adduct, a species which should also be unbound.

Conclusions

We have examined the reactions of $o\text{-}C_6H_4^{\bullet -}$ in the gas phase with a variety of molecules under the thermally equilibrated conditions of the flowing afterglow (in 0.3–0.7 Torr of helium). Consideration of the success or failure of proton-transfer reactions between well-characterized donor acids and $o\text{-}C_6H_4^{\bullet -}$ led to the determination of the gas-phase acidity of the phenyl radical: $\Delta G^\circ_{acid}[C_6H_5^\bullet] = 371^{+6}_{-3}$ kcal mol^{-1}, and $\Delta H^\circ_{acid}[C_6H_5^\bullet] = 379$ kcal mol^{-1}, via $\Delta S^\circ_{acid}[C_6H_5^\bullet] = 25.7$ cal mol^{-1} K^{-1}. Combination of our experimental acidity of the phenyl radical with appropriate values from the literature yielded the following new thermochemical values: $\Delta H_f^\circ[o\text{-}C_6H_4] = 105$ kcal mol^{-1}; BDE[C_6H_4–H] = 78 kcal mol^{-1}; $\Delta H_f^\circ[o\text{-}C_6H_4^{\bullet -}] = 92$ kcal mol^{-1}; HAA$[o\text{-}C_6H_4]^{\bullet -}$ = 89 kcal mol^{-1}; HA[$o\text{-}C_6H_4$] = 85 kcal mol^{-1}; IP[$o\text{-}C_6H_4$] = 9.03 eV; and PA[$o\text{-}C_6H_4$] = 201 kcal mol^{-1}. These thermochemical values, for the most part, represent a substantial improvement over values previously in the literature. In addition to behaving as a Brönsted base, $o\text{-}C_6H_4^{\bullet -}$ undergoes a number of other reactions, including electron transfer, H/D exchange, addition (adduct formation), and H_2^+ transfer. Reaction of $o\text{-}C_6H_4^{\bullet -}$ with alcohols and thiols is shown to be a competition between proton transfer and H_2^+ transfer. The *o*-benzyne radical anion was also demonstrated to undergo associative detachment reactions with dioxygen and butadiene, but we have only been able to postulate what the products are from these latter two reactions. One unanticipated observation from these studies is the facile addition of the *o*-benzyne radical anion adding to carbon dioxide to produce a stable distonic radical anion. This latter species is of particular interest because it offers the potential of examining chemistry of a reactive radical species (phenyl radical) in ion–molecule encounters where the ion component is exceptionally unreactive (benzoate anion).

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Supplementary Material Available: Tables of thermochemical values used and derived in this work and a few of the published heats of formation for *o*-benzyne (3 pages). Ordering information is given on any current masthead page.

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