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Structure and Reactivity of Benzoylnitrene Radical Anion in the Gas Phase

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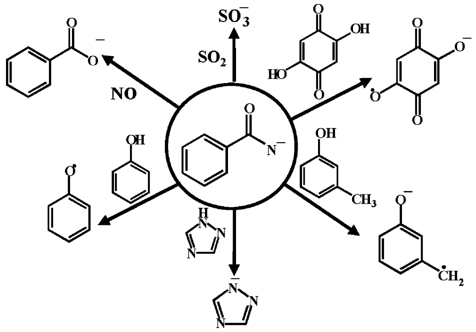
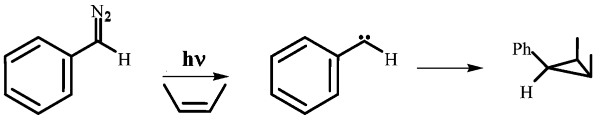


The open-shell benzoylnitrene radical anion, readily generated by electron ionization of benzoylazide, undergoes unique chemical reactivity with radical reagents and Lewis acids in the gas phase. Reaction with nitric oxide, NO, proceeds by loss of N_2 and formation of benzoate ion. This novel reaction is also observed to occur with phenylnitrene anion, forming phenoxide. Similar reactivity was observed in the reaction between benzoylnitrene radical anion and NO_2, forming benzoate ion and nitrous oxide. Electronic structure calculations indicate that the reaction has a high-energy barrier that is overcome by the energy released by bond formation. Benzoylnitrene radical anion also transfers oxygen anion to NO and NO_2 as well as to CS_2 and SO_2. In contrast, phenylnitrene anion reacts with carbon disulfide by C^+ or CS^+ abstraction, forming S^- or S_2^-. Electronic structure calculations indicate that benzoylnitrene in the ground state resembles a slightly polarized benzoate anion, but with a free radical localized on the nitrogen.

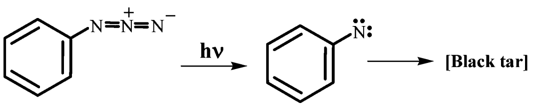
Introduction

Nitrenes are unusual molecular structures with unfilled valences that lead to high reactivity. They are closely related to carbenes in the number of valence electrons, although they usually exhibit very different reactivity.[1−3] For example, although both can be generated by photolysis of nitrogen-containing precursors,[3] phenylcarbene formed from phenyl diazomethane (PDM) reacts with alkenes to give cyclopropane (eq 1a), and, in general, reacts efficiently to form adducts with alcohols, alkenes, aromatics, and molecules with normally unreactive C−H bonds, whereas reactions of photolysis products of phenylazide with alkenes, alcohols, and aromatics generally results in formation of polymeric tar (eq 1b).[3,4] The reactivity differences result because, while both are generated in singlet (excited) states, phenyl carbene rapidly undergoes intersystem crossing (ISC) to the triplet (ground) state whereas ISC is slower in phenylnitrene such that reactivity occurs on the singlet surface.[5] In addition to being the subject of fundamental reactivity studies, nitrenes have practical uses, for example, in



(1a)

PDM



(1b)

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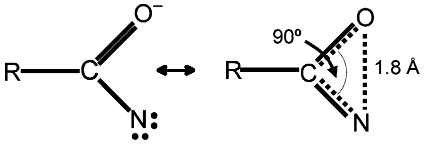
10.1021/jo701407n CCC: $37.00

labeling experiments involving biological macromolecules[6,7] and in photoresist technology.[4,8]

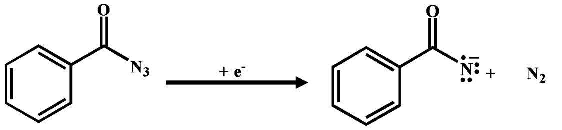
Studies have also been carried out on nitrene anions. Phenylnitrene anion, generated by electron ionization of phenyl azide,[9,10] exhibits both free radical and anionic behavior,[10] as the proton-transfer reaction with 1,1,1-trifluoroacetone and the radical displacement reaction with propionoaldehyde demonstrate its anionic and free-radical character, respectively. In addition, studies reported by McDonald et al.[9,11] show that phenylnitrene anion can undergo 1,2- and 1,4-addition reactions with various α,β-unsaturated compounds, a reaction useful in synthetic organic chemistry.[11] Most significantly, nitrene anions have been used in photodetachement[12−14] and photoelectron spectroscopic studies[15,16] to determine thermochemical properties of nitrenes.

Unlike simple alkyl- or arylnitrenes, acylnitrenes are predicted to have singlet (or nearly singlet) ground states, because the singlet states can be stabilized by resonance (eq 2).[17] B3LYP calculations carried out on benzoylnitrene by Gritsan et al.[18] and photolyses studies of naphthoyl and substituted benzoyl azides studies confirm that the acylnitrenes have singlet ground states.[19,20]



(2)

Recently we reported the formation of benzoylnitrene radical anion, $\mathbf{1}^-$, by electron ionization of benzoylazide (eq 3).[21] In our first study, we described the determination of the thermochemical properties of $\mathbf{1}^-$ and related species. In this work, we report the bimolecular reactivity of the ion and provide a description of its electronic structure.



(3)

1⁻

Experimental Section

All gas-phase ion/molecule reactions were carried out at room temperature in a flowing afterglow triple-quadrupole apparatus described previously.[22,23] Benzoylnitrene and phenylnitrene anions were generated by 70 eV electron ionization of neutral precursors, benzoylazide and phenylazide. The anions were carried by helium buffer gas (0.400 Torr, flow [He] = 190 STP cm^3/s) through the flow tube, where they were allowed to undergo ion−molecule reactions with the neutral reagent vapors added through fixed reagent inlets. The reactions were monitored by the loss of reactant ion and formation of product anion. The ions generated in the flow tube were cooled to ambient temperature by the helium buffer gas and sampled through a 1 mm orifice into a low-pressure triple-quadrupole mass filter where they were analyzed. Reaction rate constants were measured by monitoring the intensity of the reactant ion as a function of the neutral reagent flow.[22] The reaction efficiency, eff, is given by eff = $k_{\mathrm{obs}}/k_{\mathrm{coll}}$, where k_{coll} is the collision rate constant, calculated by using the average dipole orientation (ADO) method.[24]

Materials. Benzoylazide[25] and phenylazide[26] were synthesized by literature procedures. Unless otherwise indicated all the other reagents were used as received. Helium was purified through a liquid nitrogen trap containing molecular sieves. Gas purities are as follows: He (99.995%), NO (99%), NO_2 (99%), SO_2 (99%), CO_2 (99.999%), and CS_2 (99%). **Caution**: Azides are potentially explosive and should be handled with proper precautions. However, we have not encountered any problems in this work.

Computational Studies. Electronic structure calculations (B3LYP) were carried out with Gaussian 98W[27] and QChem.[28] All molecules were fully optimized with the 6-31+G* basis set. Frequency calculations were also carried out at the same level. NPA calculations[29−31] were carried out to study the charge distribution of the molecules.

Results and Discussion

(1) Electronic Structure of $\mathbf{1}^-$. The benzoylnitrene radical anion can be envisioned as arising from adding an extra electron to the triplet state of benzoylnitrene. The two singly occupied orbitals in triplet benzoylnitrene are represented in Figure 1. The a″ orbital is a carboxylate-like π orbital, whereas the a′ orbital is a σ-like orbital localized on the nitrogen. Two electronic states of the anion are created by adding an electron to either one of the orbitals in the triplet. Adding an electron to the a″ orbital creates the $^2A'$ state, which is best described as having a delocalized (carboxylate-like) anion and a localized,

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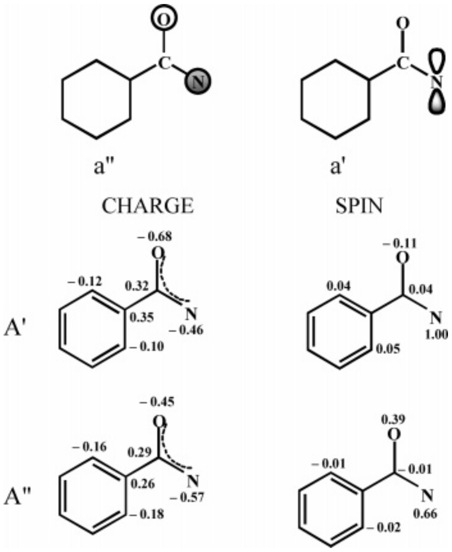


FIGURE 1. Nonbonding molecular orbitals and Mulliken charge and spin distributions of the $^2A'$ and $^2A''$ states of $\mathbf{1}^-$.

nitrogen-based radical. This picture is supported by the calculated Mulliken charge and spin densities for the ion, shown in Figure 1, which indicate a delocalized charge slightly polarized toward the more electronegative oxygen and spin density almost purely localized on the nitrogen. In contrast, adding the extra electron to the a′ orbital creates a $^2A''$ state that is a more delocalized radical with more charge on the nitrogen (Figure 1). NPA[18,29−31] calculations of the charge display the same trends as the Mulliken charges. There are only minor differences in the geometries of the two states, which are provided in the Supporting Information. At the B3LYP/6-31+G* level of theory, the $^2A'$ state is lower in energy by 28 kcal/mol, and is predicted to be the ground state. Because the calculations were carried out with the B3LYP level of theory, neither calculation suffers from spin contamination ($\langle s^2 \rangle < 0.77$).

(2) Reactivity. The observed reactivity of $\mathbf{1}^-$ reflects that expected given its electronic structure and thermochemical properties. In the section below, the reactivity is discussed according to the types of reagents. Where appropriate, the reactions are compared with those of phenylnitrene anion. Thermochemical values are calculated by using literature values.[21,32]

(a) Reactions with Radicals. Given the radical character of ion $\mathbf{1}^-$, we have investigated reactions with radical reagents NO and NO_2. Nitric oxide is a powerful reagent for investigation of open-shell anionic structures because it is a free radical but has a very small electron affinity (0.0260 ± 0.0650 eV).[33,34] Ion $\mathbf{1}^-$ is found to undergo an unexpected reaction with NO, proceeding by net addition and loss of N_2 forming benzoate anion (eq 4a). Oxygen anion transfer (eq 4b) is also observed to a lesser extent, with a branching ratio of eq 4a to eq 4b of about 5/1. The driving force for the reaction is thermochemical, as the reaction in eq 4a is exothermic by 126 kcal/mol, whereas that in eq 4b is exothermic by 21 kcal/mol. A nitrogen−oxygen exchange reaction also occurs with the phenylnitrene anion and NO (eq 4c), forming phenoxide. Reaction 4c is exothermic by 125 kcal/mol.

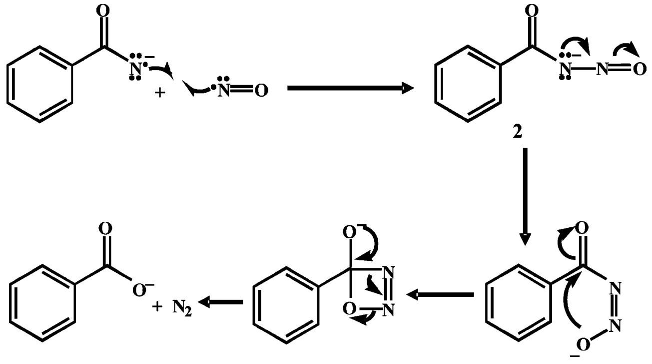
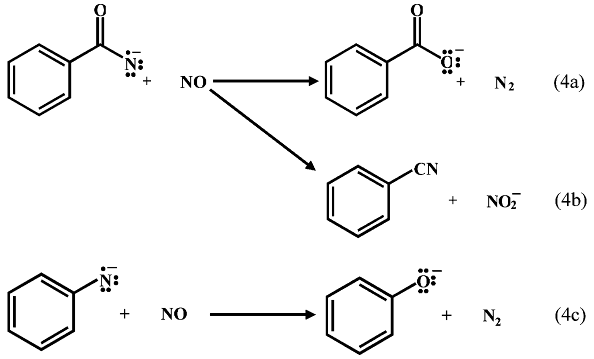


FIGURE 2. Proposed mechanism for the reaction between benzoylnitrene radical anion and NO.



Although the reactions are highly exothermic they still have high-energy barriers. The mechanism presumably involves an initial radical coupling as shown in Figure 2, to form benzoylnitrosate anion, **2**. Formation of benzoate likely proceeds through a 4-member transition state, which is calculated to be 26 kcal/mol higher in energy than the nitrosate anion. However, the transition state is still much lower in energy than the separated reactants, as the initial radical−radical coupling is exothermic by ca. 55 kcal/mol. The calculated potential energy surface (B3LYP/6-31+G*) for the reaction between $\mathbf{1}^-$ and NO is shown in Figure 3. The barrier is slightly higher for reaction of phenylnitrene anion (41 kcal/mol), but because the radical coupling is more exothermic (72 kcal/mol), the transition state energy is still well below the energy of the reactants. Because of the large barrier, the reaction between $\mathbf{1}^-$ and NO is not as efficient as would be expected given the large exothermicity, with eff = 0.15. Thus, reaction only occurs on approximately 15% of all collisions.

The nitrogen−oxygen exchange reaction observed with NO is also found to occur with NO_2 (eq 5a). In this case, the reaction is exothermic by 93 kcal/mol, leading to formation of N_2O and benzoate anion, whereas phenoxide formation in the reaction with phenylnitrene anion is exothermic by 92 kcal/mol. The mechanism is presumably similar to that shown in Figure 2, with initial formation of the phenylnitroso anion, followed by rearrangement. The phenylnitroso anion has previously been proposed to be formed in the reactions of phenyl anion with nitrous oxide[35] and deprotonated aniline with neopentylnitrite,[36] and has been shown to produce phenoxide when activated.[36]

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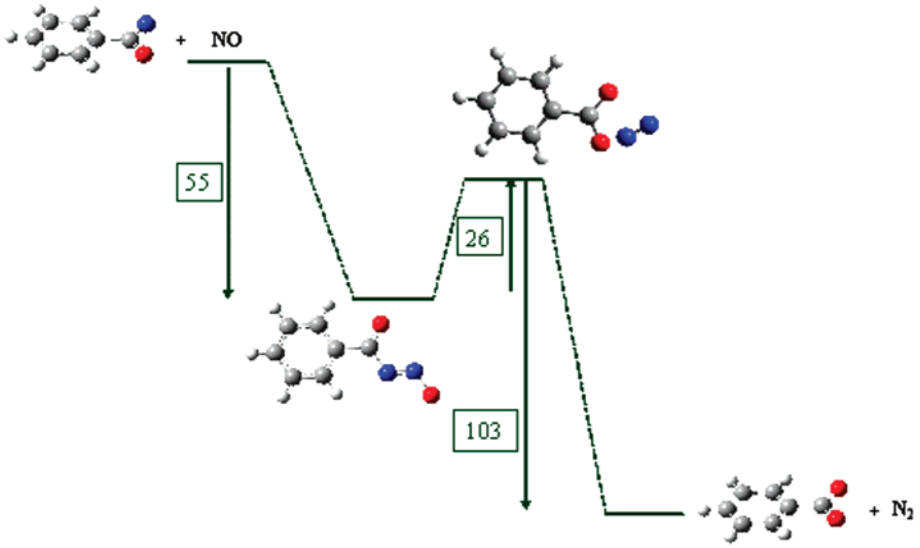
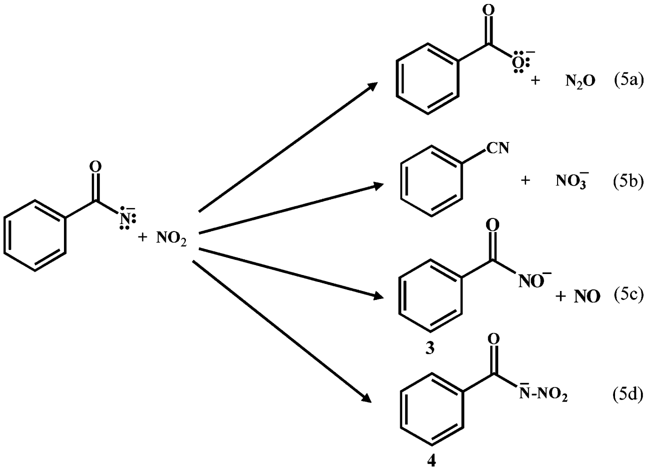
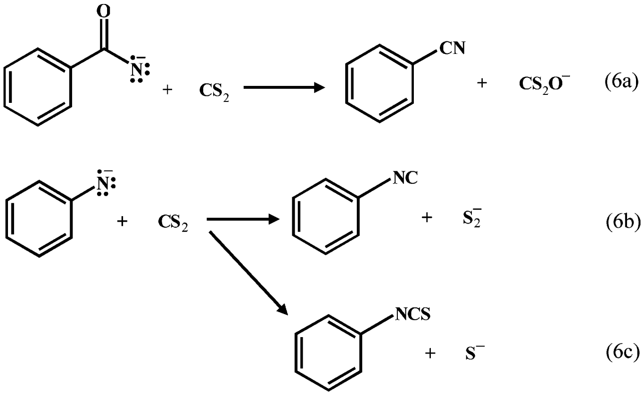


FIGURE 3. Potential energy surface for the reaction between benzoylnitrene anion and NO calculated at the B3LYP/6-31+G* level of theory. All values are 298 K enthalpies (in kcal/mol). Energies of reactants and products are the sum of the two individual species, and are not corrected for Basis Set Superposition Error.

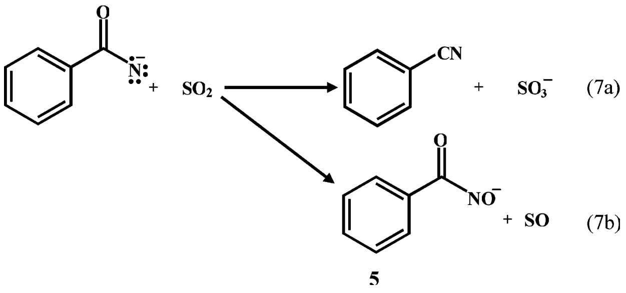
Other products formed in the reaction with **1**$^-$ include NO_3^- (eq 5b), nitrosobenzoyl anion, **3** (eq 5c), and the adduct, nitrobenzoyl anion, **4** (eq 5d), although each are formed to a much smaller extent (2%, 5%, and 17%, respectively).



(b) Reactions with Lewis Acids. Benzoylnitrene radical anion is unreactive with CO_2 or N_2O. Reaction with CS_2 leads to formation of CS_2O^-, resulting from oxygen anion transfer (eq 6a). The formation of CS_2O^- in this reaction indicates that the O^- affinity of CS_2 must be greater than the strength of the C−O$^-$ BDE in **1**$^-$, 78 kcal/mol.[21] The analogous reaction with CO_2 (to form benzonitrile and CO_3^-)[37] is endothermic by 22 kcal/mol, and therefore is not observed. Interestingly, this also means that the reverse reaction, transfer of O^- from CO_3^- to benzonitrile to give **1**$^-$, is exothermic by 22 kcal/mol. Unfortunately, no reaction was observed between CO_3^- and benzonitrile in the flow tube, suggesting the presence of a barrier to oxygen ion transfer. Oxygen ion transfer is obviously not observed in the reaction of CS_2 with phenylnitrene anion and instead, the ionic products are S^- and S_2^- with an intensity of 25% and 75%, respectively. Isonitrile and isothiocyanate products could be formed directly (eqs 6b and 6c), whereas formation of benzonitrile and the thiocyanate requires rearrangement.



Reaction between SO_2 and **1**$^-$ occurs via oxygen ion transfer to yield formation of $SO_3^-$and benzonitrile. This reaction is exothermic by 23 kcal/mol (eq 7a). In addition, oxygen atom transfer from SO_2 to give anion **5** (eq 7b) is also observed. The branching ratio between eq 7a and eq 7b is about 5/3.



(c) Proton and Hydrogen Atom Transfer. In our previous study,[21] we reported that **1**$^-$ undergoes proton transfer with

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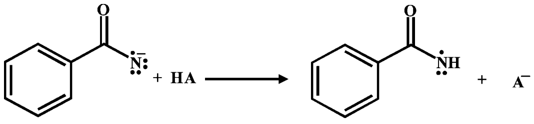
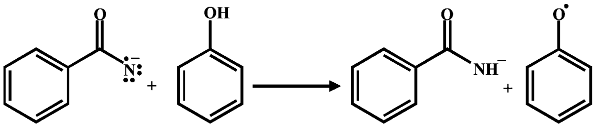
pyruvonitrile and more acidic substrates (eq 8). On the basis of proton-transfer bracketing studies the gas-phase acidity of benzamidyl radical, **1H**, was assigned $\Delta H_{\mathrm{acid}}(\mathbf{1H}) = 347 \pm 3$ kcal/mol.



(8)

1H

Phenols were found to react with $\mathbf{1}^-$ by hydrogen atom transfer (HAT) to form benzamidyl anion, $\mathbf{1H}^-$ (eq 9). On one hand, the reaction is not surprising because hydrogen atom transfer is exothermic by ca. 6 kcal/mol. However, exothermicity is not sufficient to account for the reaction because HAT does not occur with toluene and aniline despite the fact the C−H BDE in toluene[38,39] and the N−H BDE[40] in aniline are essentially the same as the O−H BDE in phenol.[40]



(9)

$\mathbf{1H}^-$

Other reagents that were found to undergo HAT with $\mathbf{1}^-$ include acetic acid and *p*-hydroquinone.

(d) H_2^+ Transfer Reactions. In select cases benzoylnitrene radical anion can react by H_2^+ transfer to form other types of interesting ions, such as ionized diradicals and carbenes. These reactions are similar to the H_2^+ transfer reactions observed for atom oxygen anion,[41] except that they occur with reagents more acidic than those that react in this manner with O^-.

The H_2^+ transfer reactions were observed with substituted phenols, including cresols and hydroquinones and other oxygen and non-oxygen containing substrates such as acetic acid, forming acetate radical, 1,1,1,3,3,3-hexafluoro-2-propanol, giving hexafluoro acetone ketyl anion, and malononitrile, forming dicyanocarbene anion. A more complete description of the H_2^+ transfer reactions has been provided elsewhere.[42]

Conclusions

The benzoylnitrene radical anion is an unusual anion with unusual reactivity. On one hand, it resembles a benzoate anion, and the thermochemical properties are consistent with what is expected given the difference between a nitrogen as opposed to an oxygen atom.[21] However, the presence of the radical leads to reactions not observed for benzoate. Radical−radical coupling is found to occur with radical reagents NO and NO_2, followed by a nitrogen−oxygen exchange reaction. This type of reactivity is also observed with phenylnitrene anion. However, benzoylnitrene radical anion also undergoes oxygen anion (O^-) transfer with many reagents, a reaction that phenylnitrene anion cannot do, and the reaction is observed with NO, NO_2, CS_2, and SO_2.

Benzoylnitrene radical anion is found to undergo hydrogen atom transfer with substituted phenols. For phenols that contain another acidic position, H_2^+ transfer is observed, leading to the formation of oxygen-based distonic radical anions, and the reaction can be used to generate other ionized reactive intermediates.

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Supporting Information Available: Experimental procedures for the synthesis of benzoyl- and phenylazide, along with NMR shift data, optimized structures and energies for all of the species calculated in this work, and full citations for references 26 and 27 are available as Supporting Information. This material is free of charge via the Internet at https://pubs.acs.org.

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