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Reactivity of 3- and 4-pyridinylnitrene-*n*-oxide radical anions

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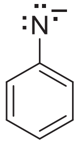
ABSTRACT

Ion–molecule reactions in a flowing afterglow are used to examine the electronic structure of 3- and 4-pyridinylnitrene-*n*-oxide radical anions. Reactions with nitric oxide are generally similar to those reported previously for other aromatic nitrene radical anions. In particular, phenoxide formation by nitrogen–oxygen exchange is observed with both isomers. Oxygen atom abstraction by NO is also observed with both isomers. Very significant differences in the reactivity are observed in the reactions of the two isomers with carbon disulfide. The reactivity of the 3-*n*-oxide isomer with CS_2 is similar to that observed previously for nitrene radical anions, and reactions of the *n*-oxide moiety are not observed, similar to what is expected based on solution chemistry. The 4-*n*-oxide isomer, however, undergoes many reactions, including oxygen atom and oxygen ion transfer and sulfur–oxygen exchange, that involve the *n*-oxide oxygen. The increased reactivity of the oxygen is attributed to increased charge density at the oxygen due to pi electron donation of the nitrene anion in the *para* position.

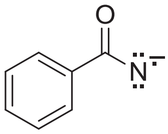
1. Introduction

Nitrene radical anions are a fascinating class of hypovalent ions. Despite their unusual electronic structures, isoelectronic with carbene radical anions [1–6], they are surprisingly easily generated in mass spectrometry, cleanly and in high abundance, by simple electron ionization of azide-substituted precursors [7–20]. Although azides are considered potentially explosive, given the recent interests in azides as reagents in “click” chemistry [21–24] they are commonly being synthesized and utilized in chemical applications, and, in principle, any of these derivatives could be used as precursors of nitrene radical anions. However, despite how easily the ions are to form, few studies of nitrene radical anions have been reported, and many of those reported have focused on the use of the anions as precursors for photoelectron/photodetachment spectroscopy studies of the corresponding nitrenes [9–14].

Nevertheless, some studies have addressed issues of electronic structures of nitrene radical anions. The simplest nitrene radical anion, HN^-, has been well-studied experimentally [25–31] and computationally [32]. Isoelectronic with OH, the HN^- ion is found to have a $^2\Pi$ electronic ground state. Ellison and co-workers [14] discussed the electronic structure of methyl nitrene radical anion, CH_3N^-, which has a ^2E ground state, but, like CH_3O, undergoes a Jahn–Teller distortion [33,34].



PhN$^-$



BzN$^-$

The electronic structures of phenylnitrene anions have been discussed in the context of photoelectron [12,13] and photodetachment [9–11] spectroscopy studies, and have been examined by electronic structure calculations [13]. The planar phenylnitrene anion, **PhN**$^-$, has an electronic structure that consist of three electrons in the two non-bonding molecular orbitals (NBMOs) of **PhN**, which consist of an in-plane, σ orbital, and a benzylic-like π orbital (Fig. 1). Unlike the case in C_{3v} methylnitrene, the orbitals in **PhN** are not degenerate, and therefore there are two possible electronic states that can be created, corresponding to $\sigma^2\pi$ ($^2B_2$) and $\pi^2\sigma$ ($^2B_1$). For substituted systems where the symmetry of the system is reduced to C_s, the electronic states correspond to $^2A''$ and $^2A'$, respectively. B3LYP calculations with large basis sets predict that the ground states of **PhN** and chloro-substituted derivatives [13] are all $\pi^2\sigma$, with the $\sigma^2\pi$ states lying approximately 0.5 eV higher in energy.

Benzoylnitrene radical anion, **BzN**$^-$, has been examined computationally and experimentally [18–20]. Like **PhN**$^-$, the ground state of **BzN**$^-$ is predicted to be $\pi^2\sigma$ ($^2A'$), but the relative energy of the $\sigma^2\pi$ state (28 kcal/mol) is predicted [18] to be much higher than that in **PhN**$^-$, reflecting a greater preference for the

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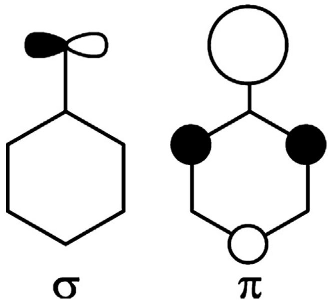
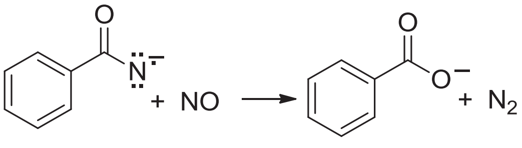


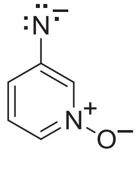
Fig. 1. Non-bonding molecular orbitals in phenylnitrene.

carboxylate-like anion over having the charge localized on a nitrogen σ orbital. Chemical reactivity of the **BzN**⁻ is consistent with the open-shell structure. In particular, reaction with NO results via radical–radical coupling to give nitrogen/oxygen exchange (Eq. (1)), leading to the formation of benzoate anion and N_2.

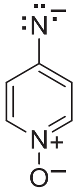


BzN⁻ (1)

In this study, we report an investigation of the reactivity of the 3- and 4-pyridinylnitrene-*n*-oxide radical anions, **3PNO**⁻ and **4PNO**⁻, respectively. The pyridine-*N*-oxide is an interesting structural motif. The formal pyridinium can nominally be viewed as an electron-acceptor, but the adjacent oxide can act as a π donor, such that the electronic effect of the *N*-oxide is dependent on the extent of benefit that can be created, via electron donation or acceptance. However, the resonance effect of the *n*-oxide can only occur with the nitrene nitrogen at the 4-position, and not at the 3-position. Moreover, for **4PNO**⁻, there are two types of stabilization that can be envisioned to result from interaction between the nitrene radical anion and the *N*-oxide, shown in Fig. 2. In the $\pi^2\sigma$ state, the pyridinium can serve as an electron pair acceptor, and the system can potentially be stabilized by contribution from the quinone-like structure. Similarly, the $\sigma^2\pi$ state can be stabilized by radical delocalization, creating a highly stable nitroxyl radical. Electron delocalization in either state is such that it eliminates the formal charge separation of the *n*-oxides, which could provide additional stabilization.



3PNO⁻



4PNO⁻

We have carried out a computational study of the electronic structures of **3PNO**⁻ and **4PNO**⁻, and an experimental investigation of their reactivity. Surprisingly, despite the possible interactions between the nitrene radical and *N*-oxide in **4PNO**⁻, we do not find significant differences in the computed electronic structures or reactivities of the two isomers in the reaction with NO. However, a dramatic difference between the ions is found in the reaction with CS_2, as the 4-isomer undergoes reactivity that is not observed for the 3-isomer, attributed to differences in accessibility of the oxide end of the ion toward reaction. The results indicate that the resonance interaction between the nitrene anion center and the *n*-oxide increases the nucleophilicity of the oxygen in the *n*-oxide moiety.

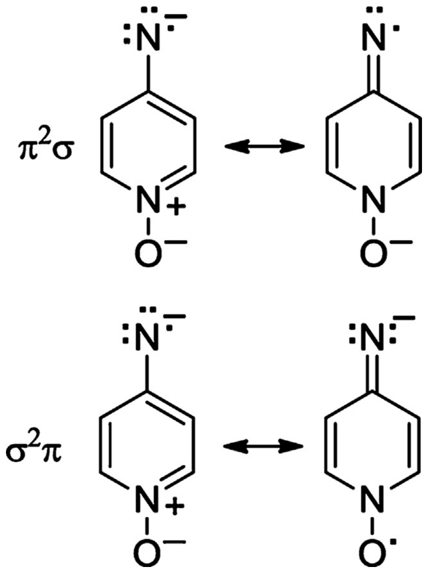


Fig. 2. Resonance structures of the $\Pi^2\sigma$ and $\sigma^2\Pi$ states of **4PNO**⁻.

2. Methods

2.1. Experimental procedures

The flowing afterglow used in the investigation has been previously described [35]. Briefly, **3PNO**⁻ and **4PNO**⁻ radical anions are generated in upstream end of flow tube by electron ionization of corresponding azide precursor. The ions are cooled to ambient temperature (298 K) and carried downstream by helium buffer gas (0.400 Torr, flow (He) = 190 STP cm^3/s), and are allowed to undergo ion–molecule reaction with neutral reagent vapors. The product ions are sampled through a 1 mm orifice into a low-pressure triple–quadrupole mass filter and detected with an electron multiplier. Reactions with mass selected ions can be carried out in the second quadrupole (Q2). Reactions in Q2 were used to verify the reaction products observed in the flow tube. In these experiments, the Q2 dc pole offset was kept very low (~1–2 V, laboratory frame) to minimize the possibility of translationally driven reactions. The energy dependencies of the observed reaction products were examined to ensure that their intensities are maximized at nearly thermal collision energies and drop off at higher energies as expected for exothermic processes.

Reaction kinetics are determined by monitoring the depletion of reactant ion as a function of neutral flow rate for sample introduced at a fixed distance from the nose cone. Pseudo-first order reaction rate constants, k_{rxn}, are obtained from a logarithmic plot of ion depletion vs reagent flow rate. Reaction rates are reported as reaction efficiencies (eff), which are the ratios of the measured rate constant to the collisional rate constant, k_{coll}, calculated by using the parameterized-trajectory method described by Su and Chesnavich [36]. Absolute uncertainties in measured rate constants are estimated to be ±50%. Branching ratios in reactions with multiple observed products are determined by measuring the branching ratios at multiple neutral flow rates, and extrapolating to zero reagent flow. Uncertainties in branching ratios are estimated to be ±10% on an absolute basis.