

New Approach to Carbene Chemistry *via* Distonic Carbene Ions. A Case of Spin-Forbidden Proton Transfer and Carbene–Biradical Tautomerism

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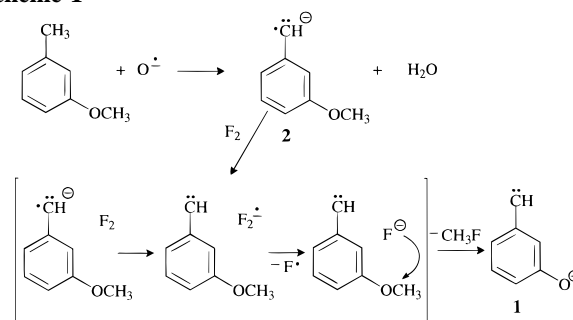
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A key strength of gas-phase ion chemistry is that it provides a means for characterizing reactive intermediates such as carbocations, carbanions, and radical ions that may be difficult or impossible to study in solution. Recent advances in gas-phase ion synthetic methods have also made it possible to investigate the chemistry of *neutral* reactive intermediates, such as free radicals and biradicals, by means of the corresponding “distonic” ions.¹ In these species, the charged and radical or biradical moieties are formally separate, and when the charged site is chemically inert, reactions of the radical or biradical portion of the molecule can be observed. Free radical reactions of distonic radical cations^{2–5} and anions^{6–9} have been investigated by several groups. We reported the generation of distonic biradical anions in the gas phase and a characterization of their spin-state-dependent reactivity.¹⁰ Distonic biradical cations were described recently by Kenttämaa and co-workers.¹¹ The next logical addition to this growing family of reactive intermediates is the *distonic carbene ion*, i.e., a gaseous ion containing a neutral carbene moiety.¹² We report here the generation of such a species by rational gas-phase synthesis and the investigation of its chemical reactivity and acid–base properties. The new distonic carbene ion is (3-oxyphenyl)methylene anion (**1**), in which a relatively unreactive phenoxide charge site is incorporated into phenylcarbene.

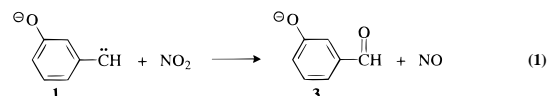
The synthesis of **1** combines the well-known propensity of atomic oxygen anion for H₂⁺ abstraction from neutral organic compounds,¹³ with the unique reactivity of molecular fluorine toward organic anions.⁶ Reaction of 3-methylanisole with O[−] in a flowing afterglow–triple-quadrupole apparatus¹⁴ yields a mixture of product ions arising mainly from proton transfer and H₂⁺ abstraction (Scheme 1).¹⁵ Reactivity studies show the H₂⁺ abstraction product to be a mixture of isomers, with the carbene

Scheme 1

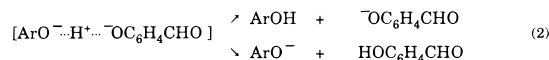


anion **2** as the major component.¹⁶ Addition of a dilute mixture of F₂ in helium to the flow tube results in rapid disappearance of **2** and formation of a product ion with the formula C₇H₅O[−]. This product is assigned the distonic carbene ion structure, **1**, based on its characteristic reactivity and the results of the authentication experiments described below. The mechanism for its formation (Scheme 1) involves dissociative electron transfer from **2** to F₂ within the ion/molecule collision complex,⁶ followed by nucleophilic attack by F[−] at the methyl group of the nascent carbene.

Ion **1** displays typical carbene reactivity,¹⁷ as well as some new reactions. Of particular significance is the O-atom transfer¹⁸ that occurs when **1** reacts with NO₂ (eq 1), since the



putative product of this reaction, **3**, is an ordinary organic ion with a readily verifiable structure. That is, **3** represents a convenient derivative for use in identifying the structure of **1**. We have used the kinetic method¹⁹ to demonstrate that derivative **3** is identical to authentic 3-oxybenzaldehyde anion, which is easily prepared by reacting F[−] with 3-methoxybenzaldehyde. Both ions react with substituted phenols to form proton-bound cluster ions that undergo collision-induced dissociation (CID) to produce *identical* yield ratios for the two different phenoxide ion fragments (eq 2). This formally equates the structures of derivative **3** and 3-oxybenzaldehyde anion, thereby confirming the structural assignment for ion **1**.



In addition to O-atom abstraction from NO₂, **1** abstracts a sulfur atom from CS₂ and COS, and it undergoes cycloaddition with electron-deficient alkenes such as CH₂=CHCN²⁰ but is unreactive toward nonpolar alkenes such as CH₂=CH₂. Ion **1** does not react with O₂ in the flow tube, but it does react by addition/OH-loss at elevated collision energies in the triple-quadrupole analyzer with an apparent onset of about 10 kcal/

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(15) The H⁺ and H₂⁺ abstraction products are formed in a *ca.* 1:3 yield ratio; other primary products (<5% yield) include [−]OC₆H₄CH₂[−] (*m*-quinomethane anion) and CH₃C₆H₄O[−] (*m*-cresolate anion).

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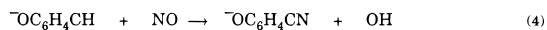
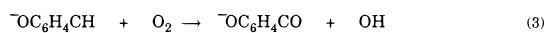
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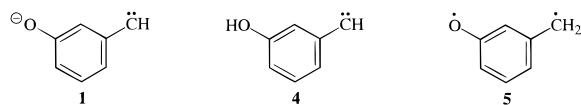
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mol (eq 3). Nitric oxide reacts with **1** by addition and by a novel N-atom transfer reaction to yield 3-cyanophenoxide ion (eq 4). A full account of the reactivity of **1** and related species will be published.²¹



An issue of obvious significance is the ground-state multiplicity of **1**. Phenylcarbene is known from experiment²² and theory²³ to be a triplet with singlet–triplet (S–T) splitting of about 5 kcal/mol. The chemical reactivity of **1** is suggestive (but not necessarily definitive) of a singlet state. Cycloadditions with electron deficient alkenes and S-atom abstraction from CS₂ are signature reactions of nucleophilic singlet carbenes,¹⁷ and the apparent barrier for reaction of **1** with oxygen is also consistent with a singlet state.²⁴ In fact, B3LYP/cc-pVTZ calculations predict a singlet (¹A') ground state for **1**, with the lowest triplet (³A'') lying 3 kcal/mol higher in energy.²⁵ The strong π -donor effect of the oxy anion substituent on the phenyl group raises the energy of the 4a'' orbital, which preferentially stabilizes the singlet state of the carbene.

Perhaps the most interesting aspect of **1** is its acid–base chemistry. Whereas anion **1** is likely to be a singlet, the neutral conjugate acid, (3-hydroxyphenyl)methylene (**4**), is calculated



at the B3LYP/cc-pVTZ level of theory to have a triplet ground state (³A''), with a S–T gap of 6.4 kcal/mol.²⁵ Organic conjugate acid–base pairs with different spin multiplicities are exceedingly rare.²⁶ Proton transfer reactions of such systems are of special interest, since they are formally spin-forbidden processes that may be associated with a barrier on the adiabatic potential energy surface. The magnitude of this barrier will depend upon the S–T splittings of the conjugate acid–base pair and the extent of spin–orbit coupling at the diabatic surface crossing. For the present system, four different spin-state pairings are possible in the conversion of anion **1** to its conjugate acid (**1** → **4**) by protonation at oxygen: (S → T), (S → S), (T → T), and (T → S). B3LYP/cc-pVTZ calculations, carried out with an isodesmic reaction approach for added accuracy,²⁷ give the values 343.6, 337.2, 346.7, and 340.3 kcal/mol, respectively, for these reaction enthalpies. We have determined an accurate proton affinity for carbene **1** by the kinetic method. Proton-bound clusters of **1** with several different phenols were formed,

(20) That the observed **1** + CH₂=CHCN addition product is a covalently bonded cycloadduct and not an electrostatically bonded cluster is inferred from the accompanying formation of a product ion, C₁₀H₇N⁺, which corresponds to HCN elimination from the adduct. This is consistent with the high exothermicity of a carbene/alkene cycloaddition reaction.

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(25) Geometry optimizations and vibrational analysis carried out at the B3LYP/cc-pVDZ level. All species were found to possess planar structures. The computed S–T gap for phenylcarbene at the B3LYP/cc-pVTZ/B3LYP/cc-pVDZ level is 6.2 kcal/mol, in good agreement with other theoretical values.

(26) Examples of organic systems with this property are singlet nitrenium ions and triplet nitrenes (RNH⁺/RN); singlet carbenes and triplet carbyne anions (RCH/RC⁻). An organic biradical system of this type was recently reported: Ishiguro, K.; Ozaki, M.; Sekine, N.; Sawaki, Y. *J. Am. Chem. Soc.* **1997**, *119*, 3625. A novel inorganic example is described in: Janaway, G.; Zhong, M.; Gate, G. G.; Chabinye, M. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1997**, *119*, in press.

and the ratios of phenoxide ion fragments resulting from CID of these clusters were determined. Analysis of the semilogarithmic relationship¹⁹ between the yield ratios and the known acidities of the phenols gives a proton affinity for **1** of 343.0 ± 0.5 kcal/mol, where the uncertainty is determined in the manner described previously.²⁸ This is in excellent agreement with the value predicted by the calculations for protonation of singlet **1** to give triplet **4** (343.6 kcal/mol) but is significantly different from the values predicted for any other spin-state interconversions. We take this as strong support for the assignment of a singlet ground state for carbene **1** and a triplet ground state for **4**. These results also suggest that the “spin barrier” for adiabatic proton transfer to ion **1** cannot be very large and that intersystem crossing must be fast on the time scale of the intermediate lifetimes.

Another notable feature of **1** is that it is an *ambident ion*, capable of undergoing protonation either at the oxygen to produce **4**, or at the carbene carbon to yield *m*-benzoquinomethane, **5**.²⁹ In fact, B3LYP/cc-pVTZ calculations indicate that triplet biradical **5** is 22.6 kcal/mol lower in energy than triplet carbene **4**.³⁰ This means that, like an enolate ion, the phenolic oxygen of **1** is the kinetic protonation site, but the carbene carbon is the thermodynamic protonation site, with a basicity which is greater than that at oxygen by the **4** ⇌ **5** tautomer energy difference. The ambident character of **1** could be demonstrated qualitatively in the cluster ion CID experiments. In the series of proton-bound clusters of **1** with the phenolic reference acids that were used to evaluate the oxygen basicity, the relative yield of **1** from CID naturally increases as the acidities of the reference phenols decrease until, eventually, only ion **1** appears as a CID fragment. Remarkably, when proton-bound clusters of **1** were formed from aliphatic alcohols having 25–30 kcal/mol weaker acidities (higher ΔH_{acid}) compared to phenols, they produced significant yields (up to 30%) of alkoxide fragments as well as ion **1** when subjected to CID.³¹ In contrast, proton-bound clusters of these same alcohols with *m*-cresolate anion, CH₃C₆H₄O⁻, a model phenoxide ion that does not possess a more basic carbon site, produce only the phenoxide fragment upon CID. We therefore interpret the CID behavior of the clusters of **1** as evidence for carbon protonation and, hence, carbene–biradical tautomerism in the activated ions.³²

The synthetic approach used for ion **1** is quite flexible. We are currently using it to generate distonic carbene ions with other types of charged sites, such as carboxylates and thiolates, and with different classes of carbene, such as vinylidenes, cycloalkylidenes, and α -chlorocarbenes.

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(27) The calculated enthalpy change for the reaction **1** + C₆H₅OH → **4** + C₆H₅O⁻ was combined with the experimental acidity of phenol, $\Delta H_{\text{acid}}(\text{C}_6\text{H}_5\text{OH}) = 349.7 \pm 1.1$ kcal/mol, derived from the O–H bond energy of phenol (Tsang, W. *Heats of Formation of Organic Free Radicals by Kinetic Methods in Energetics of Organic Free Radicals*; Simoes, J. A. M., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic and Professional: London, 1996) and the electron affinity of phenoxy radical (Gunion, R.; Gilles, M. K.; Polak, M.; Lineberger, W. C. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 601.)

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(31) The mechanism for sampling the two basic sites with different reference acids is currently under investigation. Preliminary evidence suggests that the phenols and alcohols preferentially bind to the oxygen site of **1** but can rearrange to interact with the carbon site when the clusters are collisionally activated. For an example of other proton-bound clusters displaying this behavior, see: Hoke, S. H., II; Yang, S. S.; Cooks, R. G.; Hrovat, D. A.; Borden, W. T., *J. Am. Chem. Soc.* **1994**, *116*, 4888.

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