

Anion-Molecule Approaches to Non-Kekulé Molecules: The Radical Anion of Tetramethyleneethane

Jeehiun Lee,[†] Phillip K. Chou,[‡] Paul Dowd,[‡] and Joseph J. Grabowski^{*,†}

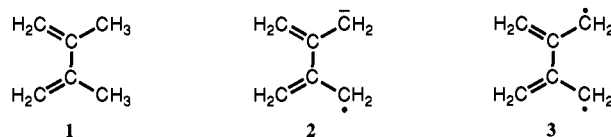
Departments of Chemistry
Harvard University
Cambridge, Massachusetts 02138
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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Gaseous cations with spatially separated radical and charge sites, "distonic" radical cations, have undergone much study¹⁻⁸ recently. Distonic radical anions⁹⁻¹¹ are less well-defined and are relatively unexamined. The interest in such species lies in their unique structure and unknown reactivity, as well as in their role as the reduced equivalents of species of long-standing interest: diradicals, or non-Kekulé molecules. We wish to report here the first example of the rational synthesis of a 1,4 radical anion by a reaction which should provide a convenient gas-phase synthesis of a large number of similar distonic radical anions. More important, the radical anion generated is that of tetramethyleneethane, thereby offering a pathway by which the electronic properties of the ground-state neutral molecule can be examined in the gas phase.

The atomic oxygen radical anion reacts rapidly with all organic compounds.¹² It possesses the unique ability to abstract a proton and a hydrogen atom from a molecule M, affording an (M - 2H)⁻ ion in a mechanism often referred to as "H₂^{•+}-transfer or -abstraction. This reaction has been used to generate and study the anionic equivalents of classical reactive intermediates of organic chemistry such as the vinylidene radical anion,¹³⁻¹⁸ the *o*-benzynes radical anion,¹⁰ and several carbene radical anions.^{16,19-22} These qualities led us to speculate that O⁻ might react efficiently

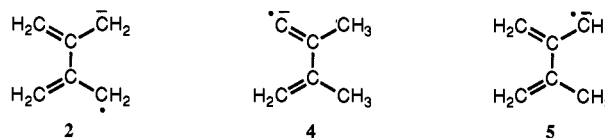
with 2,3-dimethyl-1,3-butadiene (DMB, **1**) to afford an (M - 2H)⁻ ion in high yield. DMB is of particular interest because



H₂^{•+}-abstraction from the 1,4 positions would give the radical anion (**2**) of tetramethyleneethane (TME). TME (**3**) has long been the center of a debate between theory and experiment concerning the nature of its ground state: Is it a triplet or a singlet?²³⁻²⁸ The generation of the radical anion of TME would indicate that TME possesses a positive electron affinity. Furthermore, the radical anion of TME might make it possible to determine the ground state nature of the neutral. Appropriate negative ion photoelectron spectroscopy experiments²⁹ have the potential to reveal the ground state in the gas phase, as well as to provide information about both the radical and the anion.^{30,31}

Our experiments were carried out under thermally equilibrated (298 K) conditions using the flowing afterglow technique.^{21,32} The reaction of O⁻ (generated by electron ionization of N₂O) with DMB (*k*_{obs} = (2.2 ± 0.09) × 10⁻⁹ cm³ molecule⁻¹ s⁻¹, Eff = 1)³³ affords a radical anion (M - 2H)⁻ in high yield, as well as HO⁻ and (M - H + O)⁻ in an approximate ratio of 5:4:1.³⁴ In addition to the primary processes, the newly formed HO⁻ undergoes a fast secondary reaction with a second equivalent of the parent DMB, deprotonating it to produce (M - H)⁻.

Three reasonable structures for the radical anion are a 1,4-diyli anion (**2**),⁹⁻¹¹ a vinylidene radical anion (**4**),¹³⁻¹⁸ and a carbene radical anion (**5**).^{16,19-22} To elucidate the structure of the (M -



2H)⁻ ion, we allowed it to react with various neutrals that have utility as structural probes in the gas phase. With D₂O, the radical anion undergoes eight H/D exchanges, suggesting the 1,4 radical anion structure. Furthermore, when the radical anion is allowed to react with high concentrations of N₂O, no products are observed except for a small amount resulting from nitrogen atom transfer, which is known to take place with vinylidene radical anions,¹⁸ therefore, most of the (M - 2H)⁻ cannot result from 1,1-H₂^{•+}-abstraction from a vinylic position. In order to confirm the

[†] Harvard University.

[‡] University of Pittsburgh.

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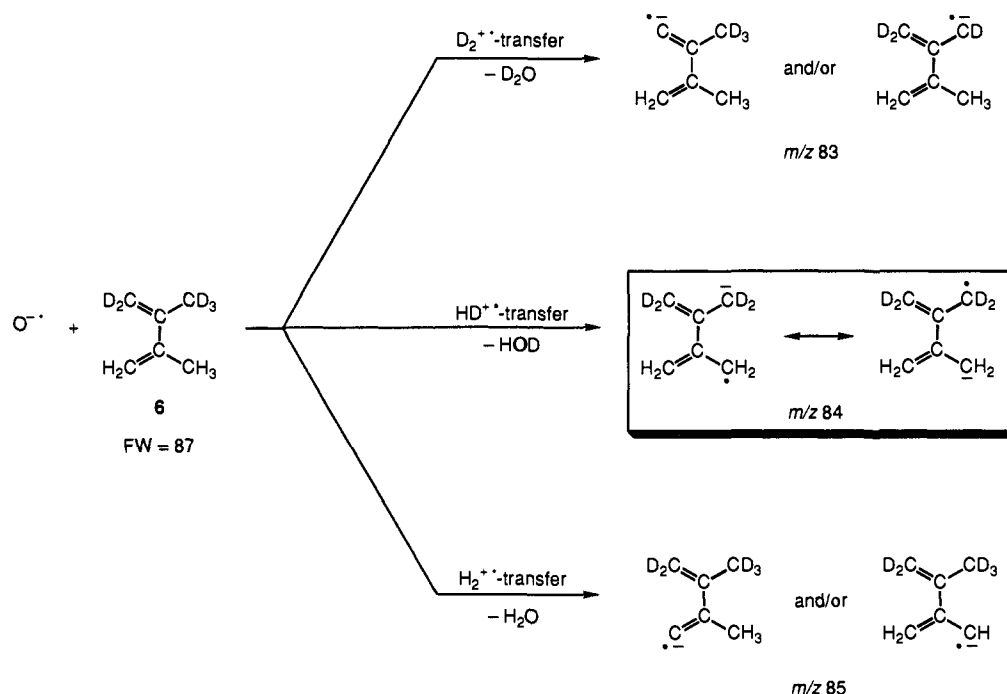
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(34) Due to the rapid nature of both primary and secondary reactions as well as the presence of small amounts of hydroxide in the reactant ion spectrum, accurate product distributions are particularly difficult to find for O⁻ reaction. More accurate numbers will be reported in the upcoming full paper.

Scheme I. Possible Structures of the Radical Anion Formed from Reaction of the Atomic Oxygen Radical Anion with 1,1-*d*₂-2-(*d*₃-Methyl)-3-methyl-1,3-butadiene



structure of the $(M - 2H)^{\bullet-}$ ion, we examined the $H_2^{+\bullet}$ -transfer pathway using the reaction of $O^{\bullet-}$ with 1,1-*d*₂-2-(*d*₃-methyl)-3-methyl-1,3-butadiene (6). The major product ion corresponds to $HD^{+\bullet}$ loss (Scheme I), proving that the greater portion of the $H_2^{+\bullet}$ -transfer product is the radical anion of TME. Because the peak corresponding to $D_2^{+\bullet}$ loss in the mass spectrum, m/z 83, is minor, we conclude that we have successfully generated the distonic radical anion of TME in high yield.

Subsequent experiments included bracketing the basicity of the TME radical anion.³⁵ Whereas the $(M - 2H)^{\bullet-}$ exchanges with D_2O yet does not deprotonate it, with CH_3OD no exchange is seen while deprotonation is observed. Furthermore, the radical anion is not observed to deprotonate the parent DMB. Additional experiments with furan, isoprene, *sec*-butyl alcohol, and acetonitrile lead us to the conclusion that the basicity of the radical anion is slightly below that of the conjugate base of isoprene (≤ 385.7 kcal mol⁻¹) (Table I, supplementary material).

In the course of our structure and reactivity studies, we often observed that the radical anion behaved unconventionally and unpredictably. For example, when allowed to react with CS_2 , the $(M - 2H)^{\bullet-}$ undergoes both sulfur atom transfer and CS_2 addition.³⁶⁻³⁸ The $(M - H)^{\bullet-}$ ion also follows addition pathways but does *not* undergo sulfur atom transfer. DePuy and co-workers³⁶⁻³⁸ have observed that with conventional anions, the *more* basic the anion, the *more* sulfur atom transfer is observed; as the anion becomes less basic, addition predominates. That the radical anion of TME, compared to the more basic anion of DMB, does *not* follow this observed trend reflects the unique reactivity of the distonic radical anion; it is not readily analyzed in light of the behavior of conventional anions.

Unpredictability and uniqueness of the radical anion's reactivity is also evident following examination of the possibility of transferring radical species to the radical site by allowing the radical anion to react with I-I and *t*BuO-*Ot*Bu. Since these

compounds have relatively weak homolytic bond dissociation energies (36.1 and 38.0 kcal mol⁻¹, respectively),³⁹ we wondered if transfer of I^{\bullet} or *t*Bu O^{\bullet} to the radical site of the radical anion would be possible—that is, could we see *radical* reactivity in this radical anion? No such transfer, however, was observed. We also examined the reaction of the radical anion with CH_3S-SCH_3 (BDE = 77.0 kcal mol⁻¹),³⁹ which has been shown to transfer CH_3S^{\bullet} to certain distonic radical cations.⁶ Again, no transfer was observed.⁴⁰ Clearly, the distonic radical anion is unique and cannot be treated as a conventional radical species or even as its cationic counterpart.

By successfully generating the radical anion of tetramethylethane in high yield, we have opened the way for further study of a unique and understudied species, the distonic radical anion. We have also shown that TME has a positive electron affinity. This species holds great promise for elucidation of the nature of the ground state of the tetramethylethane diyl, a non-Kekulé molecule of much interest to experimentalists and theoreticians.

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Supplementary Material Available: Table summarizing TME radical anion basicity bracketing; table with estimated thermochemistry for various reaction pathways; experimental protocol for the synthesis of 1,1-*d*₂-2-(*d*₃-methyl)-3-methyl-1,3-butadiene (5 pages). Ordering information is given on any current masthead page.

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(40) A unique ion is produced from this reaction, which may be the result of CH_3S^{\bullet} transfer followed by H^{\bullet} loss. Studies are underway to characterize this product ion; we know, however, that simple CH_3S^{\bullet} transfer does not take place.