J. Am. Chem. Soc. **1996,** *118,* 8871−8874

Anion-Molecule Approaches to Non-Kekulé Molecules: The Radical Anion of Cyclopentadienylidenetrimethylenemethane and Derivatives

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Received July 17, 1995. Revised Manuscript Received June 3, 1996[⊗]

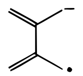
Abstract: Cyclopentadienylidenetrimethylenemethane radical anion **4**, the one-electron reduction product of the corresponding diradical **3**, was generated by a gas phase ion-molecule reaction of 6,6-dimethylfulvene (**5**) with $O^{\bullet-}$. Characterization was carried out by isotopic labeling to confirm the distonic structure of the radical anion. The results suggest that negative ion photoelectron spectroscopic experiments can be used to resolve a conflict between theories regarding the nature (singlet or triplet) of the ground state of **3**. In reactivity studies, the radical anion **4** is a better nucleophile than its corresponding anion **6**, a result similar to that found for the tetramethyleneethane radical anion **1**. The basicity of the radical anion **4** has been bracketed at approximately 354 ± 3 kcal/mol. This study contains the first evidence that a distonic radical anion can react as a radical as well as an anion, a result that will lead to further gas phase examination of the radicals in the distonic ion series.

Introduction

Distonic radical anions,[1−3] with spatially separated radical and charge sites, have unusual and distinctive properties. They can be considered as both gas phase precursors of diradicals as well as free radicals with an appended, remote charge. Negative ion photoelectron spectroscopic measurements[4−6] can determine the electron affinity and, most important, the ground state multiplicity of the derived diradicals. The presence of the anion makes the free radical, which would not normally be investigated by mass spectrometry, amenable to detection in the gas phase. The radical anions also show characteristic radical features to be described later in this paper.

Lee and co-workers[1] reported the first rational, gas phase, distonic ion synthesis of the 1,4 radical anion of tetramethyleneethane (**1**). Wenthold and co-workers[2] followed with the parent 1,3 radical anion of trimethylenemethane (**2**). The neutral triplet diradicals of both species have been subjected to extensive EPR studies in the condensed phase.[7−9] Recently, Wenthold and co-workers[10] have successfully generated the trimethylenemethane diradical from **2** in the gas phase. Using negative ion photoelectron spectroscopy, they found the singlet-triplet splitting and the heat of formation for trimethylenemethane to be in good agreement with theoretical prediction.

We report the first experimental efforts aiming at exploring the ground state of cyclopentadienylidenetrimethylenemethane (**3**). Herndon[11] first suggested that the nonalternant diradical **3** has a closed shell[12] and is predicted by simple HMO theory to be a ground state singlet. However, both semiempirical[13,14] and high-level *ab initio* calculations[15] predict **3** to be a ground state triplet. Synthesis and characterization of the radical anion **4** opens the possibility of settling this difference by experiment.



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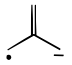

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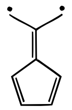

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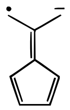

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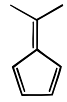

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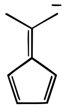

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Results and Discussion

6,6-Dimethylfulvene (**5**, hereafter identified as dimethylfulvene) is a well-studied molecule in terms of its Brönsted and Lewis acid−base properties in solution[16] and in the gas phase.[17] Dimethylfulvene **5** can also be considered to be a precursor to **3** by loss of one hydrogen atom from each methyl group. Hydrogen atom and proton abstraction from **5** in a controlled two-step process will create the radical anion **4**. Electron removal from **4** by negative ion photoelectron spectroscopy can then be used to determine the electron affinity of the diradical **3** and energy gaps to various excited states.[18]

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

(1) Lee, J.; Chou, P. K.; Dowd, P.; Grabowski, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 7902.

(2) Wenthold, P. G.; Hu, J. Squires, R. *J. Am. Chem. Soc.* **1994**, *116*, 6961.

(3) Lee, J.; Grabowski, J. J. *Chem. Rev.* **1992**, *92*, 1611.

(4) Bowers, M. T., Ed. *Ions and Light*; Academic Press: New York, 1984; Vol. 3.

(5) Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731−3732.

(6) Engleking, P. C.; Corderman, R. R.; Wendoloski, J. J.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C. *J. Chem. Phys.* **1981**, *74*, 5460−5473.

(7) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587−2588.

(8) Dowd, P.; Sachdev, K. *J. Am. Chem. Soc.* **1967**, *89*, 714−716.

(9) (a) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066−1068. (b) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416−7417.

(10) Wenthold, P. G.; Hu, J.; Squires, R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475−476.

(11) (a) Herndon, W. C.; Ellzey, M. L., Jr. *Tetrahedron Lett.* **1974**, 1399. (b) Eldin, S.; Liebman, J.; Reynolds, L. D.; Dowd, P. *Tetrahedron Lett.* **1992**, *33*, 4525.

(12) Dowd, P. *Tetrahedron Lett.* **1991**, *32*, 445.

(13) Mestechkin, M.; Vysotski, Y. *Tetrahedron Lett.* **1975**, 109.

(14) Radhakrishnan, T. P. *Chem. Phys. Lett.* **1993**, *207*, 15.

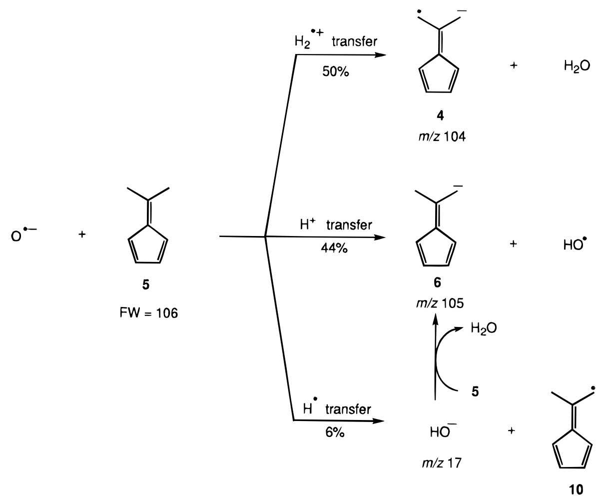
(15) Nachtigall, P.; Dowd, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 4747.

(16) (a) Yates, P. *Adv. Alicyclic Chem.* **1968**, *2*, 59. (b) Bergman, E. D. *Prog. Org. Chem.* **1955**, *3*, 81.

(17) Brickhouse, M. D.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 2706−14.

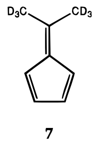
S0002-7863(95)02358-4 CCC: $12.00

Scheme 1. Pathways by Which the Atomic Oxygen Radical Anion Reacts with 6,6-Dimethylfulvene



The atomic oxygen radical anion $O^{\bullet-}$ was generated by electron ionization of trace amounts of nitrous oxide in 0.2 Torr of argon in a flowing afterglow. Reaction of $O^{\bullet-}$ with **5** produced radical anion **4** and anion **6** in an approximately 1:1 ratio (Scheme 1). The reaction is clean and rapid, and at long enough time, only **4** and **6** are present. Another primary ion product HO^- is also generated in minor amount (Scheme 1), but it undergoes rapid proton transfer with the large excess of **5** present under the pseudo-first-order reaction conditions. Thermochemical estimates for possible product channels resulting from the reaction of $O^{\bullet-}$ with dimethylfulvene are summarized in Table 1.

It is important to establish the structure of the radical anion **4**, since $O^{\bullet-}$ is known to abstract hydrogen from both *sp*^{2}- and *sp*^{3}-hybridized carbon-hydrogen bonds.[3] Carbene radical anions are also known to be produced from reaction of $O^{\bullet-}$ with methyl groups, and this path is predicted to be thermochemically accessible in the present case (Table 1). Therefore, we examined the reaction of $O^{\bullet-}$ with 6,6-dimethyl-d_6-fulvene[19] (**7**) and 6-(methyl-d_3)-6-methylfulvene (**8**). The major product from **7** corresponds to 94% loss of $D_2^{\bullet+}$, indicating that only two structures need be considered: the distonic radical anion **4** and the carbene radical anion **9**. When $O^{\bullet-}$ was allowed to react with **8**, at least[20] 82% $HD^{\bullet+}$ transfer occurred based on an isotopic purity of 92% deuterium on the labeled methyl group (Scheme 2). Thus, the distonic radical anion **4** can be produced in high yield in the gas phase.



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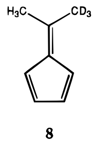

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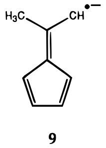

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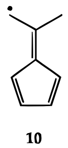

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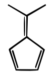
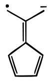
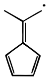
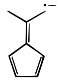
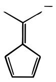
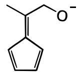
To determine the acidity of the radical **10**, it was necessary to bracket the basicity of **4**.[21] First, it was observed that **4** does not deprotonate or undergo exchange with D_2O or CD_3OD. From branching ratio analysis on the reaction of $O^{\bullet-}$ with dimethylfulvene **5** (Scheme 1), we found that **4** does not deprotonate dimethylfulvene **5**. To bracket the acidity: deprotonation occurred when **4** was allowed to react with butanethiol, but deprotonation was not observed with 1,3-cyclohexadiene, CF_3CH_2OD, acetaldehyde, or ethylene glycol. We conclude that the basicity of **4** is 354 ± 3 kcal/mol, since it lies between that of the parent anion **6** and butanethiolate. The results are summarized in Table 2.

For further characterization of **4**, we compared its reactivity and that of the dimethylfulvene conjugate base **6** with several neutral molecules. Anion **6** was obtained in pure form by deprotonation of **5** using hydroxide ion. The radical anion **4** reacts with CS_2 by sulfur abstraction (major ion at *m/z* 136) and CS_2 addition (minor ion at *m/z* 180), while anion **6** gives only CS_2 addition (*m/z* 181). For more basic carbanions such as the anions of 1,3-butadiene (PA = 397 kcal/mol) and 1-methylpyrrole (PA = 386 kcal/mol), there are two reaction channels with CS_2: addition and sulfur atom abstraction. Addition is the only reaction channel for less basic carbanions such as the anions of nitromethane (PA = 356 kcal/mol) and

Table 1. Heats of Reaction for Several Possible Pathways of the Reaction of the Atomic Oxygen Radical Anion with 6,6-Dimethylfulvene[a]

	Product Channel	$\Delta H^\circ_{rxn\,298}$ (kcal mol-1)
$O^{-\bullet}$ +  +25.8 +28.0	$\longrightarrow$ ···	
	$\xrightarrow{H_2^{+\bullet}\text{-transfer}}$  + H_2O +48.8[b] -57.8	-62.8
	$\xrightarrow{H^\bullet\text{-transfer}}$ HO^- +  -32.8 +60.4	-26.2
	$\xrightarrow{H_2^{+\bullet}\text{-transfer}}$  + H_2O 59.4[c] -57.8	-52.2
	$\xrightarrow{H^+\text{-transfer}}$  + $HO^\bullet$ +16.4 +9.3	-28.1
	$\xrightarrow{\text{Oxide formation}}$  + $O^\bullet$ -35.4[d] +9.3	-37.1

[a] All acidities taken from the following reference unless otherwise indicated: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. These data, in slightly updated form, are also available by way of: NIST Negative Ion Energetics Database (Version 2.06, January 1990), NIST Standard Reference Database 19B. [b] ΔH_f° is estimated by assuming the methyl C−H bond of the anion of 6,6-dimethylfulvene (ΔH_f° = 16.4 kcal mol^{-1}) has the same bond dissociation energy as that of 6,6-dimethylfulvene (BDE = 84.5 kcal mol^{-1}). [c] ΔH_f° is estimated using the heat of formation of the anion of 6,6-dimethylfulvene (ΔH_f° = 16.4 kcal mol^{-1}), the carbene anion of acetonitrile (ΔH_f° = 68.2 kcal mol^{-1}), and the anion of acetonitrile (ΔH_f° = 25.2 kcal mol^{-1}). [d] ΔH_f° is estimated using the heat of formation of the anion of 6,6-dimethylfulvene (ΔH_f° = 16.4 kcal mol^{-1}), allyl anion (ΔH_f° = 29.9 kcal mol^{-1}), and the anion of 2-propenol (ΔH_f° = −21.9 kcal mol^{-1}).

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[18] Ervin, K. M.; Lineberger, W. C. In *Advances in Gas Phase Ion Chemistry;* Adams, N. G., Babcock, L. M., Eds.; JAI: Greenwich, CT, 1992; pp 121−166.

[19] Gajewski, J. J.; Paul, G. C.; Chang, M.; Gortva, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 5150.

[20] Isotopic scrambling is a known process in similar reactions involving $O^{\bullet-}$. See: Matimba, H. E. K.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Soc. Mass. Spectrom.* **1993**, *4*, 73−81.

[21] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

Scheme 2. Reaction of Atomic Oxygen Radical Anion with 6-(Methyl-d_3)-6-methylfulvene

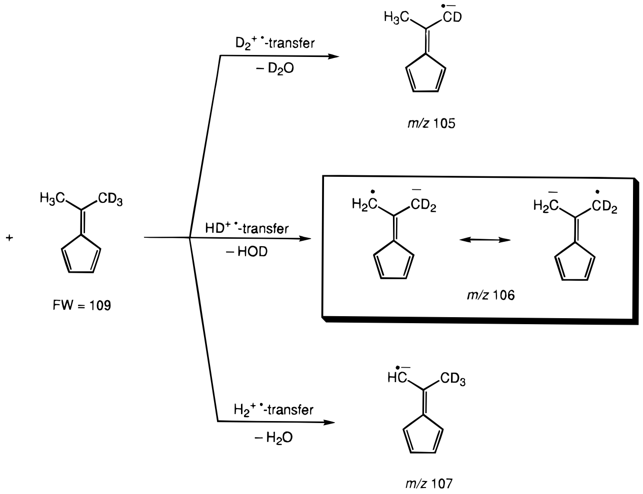


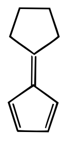
Table 2. Results from Qualitative Experiments on Gas-Phase Reactions of the Radical Anion of CPTMM$^{\bullet-}$ with a Series of Bronsted Acids at 298 K[a]

acid (AH)	ΔH°_{acid})[HA] (kcal mol^{-1})	ΔH°_{acid}HA] (kcal mol^{-1})	Is PT observed?
D_2O	392.0	386.1	no
CD_3OD	383.5	376.9	no
1,3-cyclohexadiene	373.3	356.8	no
acetaldehyde	365.8	359.0	no
ethylene glycol	365.1	360.9	no
CF_3CH_2OD	361.8	354.1	no
6,6-dimethylfulvene	354.1	347.5	no
CPTMM$^{\bullet-}$	354 ± 3		this work
butanethiol	353.7	347.4	yes

[a] See Table 1, footnote *a*.

diazomethane (PA = 373 kcal/mol).[22-24] Sulfur atom transfer observed with distonic radical anions **4** (PA = 354 kcal/mol) and **1**[1] (PA ≤ 385 kcal/mol) suggests that distonic radical anions are better nucleophiles than the closed shell anions of similar structure and basicity. This is supported by the observations that CO_2 adds to radical anion **4** but does not react with anion **6**. Likewise, O_2 does not react with **6** but reacts with **4** to give a reactive electron detachment product as do many radical anions. Coupling of radical anion **4** with nitric oxide also gives an adduct (*m/z* 134).[25] Abstraction by **4** of a fluorine atom from F_2 (BDE = 37.83 kcal mol^{-1})[26] to form *m/z* 123 and of $CH_3S^\bullet$ from CH_3S-SCH_3 (BDE = 77.0 kcal mol^{-1})[26] also indicates the unique radical character of **4**.[27] The radical anion **4** does not react with N_2O, in accord with the pattern established for closed shell anions.[28]

Tetramethylenefulvene (**11**) and 6,6-diethylfulvene (**12**) react with $O^{\bullet-}$ to give the corresponding radical anions **11**$^{\bullet-}$ (*m/z* 130) and **12**$^{\bullet-}$ (*m/z* 132) in good yields (>35% of reaction products). Thus, this method has the potential of producing an extended series of nonalternant, distonic radical anions. The clean reactions observed in all cases will be important for future negative ion photoelectron spectroscopic measurements.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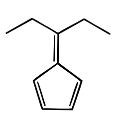
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Experimental Section

General. All condensed-phase reactions were conducted under an Ar atmosphere in oven-dried glassware. Acetone-d_6 and *n*-butyllithium (Aldrich, 1.6 M in ether) were used without further purification. 1,3-Cyclopentadiene was distilled from dicyclopentadiene. Acetone-1,1,1-d_3 was synthesized by oxidizing 2-propanol-1,1,1-d_3 with ozone[29] at 0 °C. Tetrahydrofuran was distilled from sodium/benzophenone immediately prior to use. ^{1}H, ^{2}H, and ^{13}C NMR were obtained at 300, 76.8, and 75.1 MHz, respectively. All chemical shifts are reported in ppm.

2-Cyclopentadienyl-2-hydroxypropane-d_6. Freshly distilled cyclopentadiene (11.50 g, 0.174 mol) was dissolved in 150 mL of THF and cooled to −78 °C in an acetone/CO_2 bath. *n*-BuLi (1.6 M in hexanes, 109 mL, 0.174 mol) was added dropwise under an Ar atmosphere over 35 min. The mixture was stirred for 2 h before acetone-d_6 (5.5 g, 49 mmol, 99.9% D) was added swiftly. Methanol (30 mL) was added 5 min later. After stirring for an additional 30 min, the partially frozen mixture was poured into 150 mL of ice water. Three 150-mL portions of ether were used for extraction. The combined organic layers were washed with three 150-mL portions of ice water. The organic layer was dried over $MgSO_4$, filtered, and concentrated to 8.0 g of yellow oil. The crude product was purified on silica gel, eluted with 20% ethyl acetate in hexanes. The product alcohol was obtained as 4.0 g (36%) of a yellow oil. It was a 51:49 mixture of 2-(1′-cyclopentadienyl)-2-hydroxypropane-d_6 and 2-(2′-cyclopentadienyl)-2-hydroxypropane-d_6 isomers.

^{1}H NMR ($CDCl_3$): one isomer showed δ 1.76 (s, 1 H), 2.96 (m, 2 H), 6.16 (m, 1 H), 6.46 (m, 1 H), 6.60 (m, 1 H); the other isomer showed δ 1.78 (s, 1 H), 3.02 (m, 2 H), 6.33 (m, 2 H), 6.41 (m, 1 H). ^{13}C NMR ($CDCl_3$): one isomer had δ 29.6 (septet, J = 19 Hz), 40.1 (t, J = 126 Hz), 70.3 (s), 123.9 (d, J = 173 Hz), 131.87 (d, J = 136 Hz), 131.94 (d, J = 134 Hz), 156.2 (s); the other isomer had δ 28.7 (septet, J = 19 Hz), 41.0 (t, J = 121 Hz), 69.7 (s), 125.2 (d, J = 161 Hz), 131.7 (d, J = 153 Hz), 134.2 (d, J = 171 Hz), 154.6 (s). ^{2}H NMR ($CHCl_3$): δ 1.42 (br s). IR (neat) 3355 cm^{-1} (OH). MS *m/z* (relative intensity) 130 (M$^+$, 35), 112 (97), 94 (35), 84 (100), 65 (19). HRMS calcd for $C_8H_6D_6O$: 130.1265. Found: 130.1269. The labeled methyl groups contain 99% deuterium based on mass spectral analysis in which d_6:d_5 = 100:9.

6,6-Dimethyl-d_6-fulvene (7). Under 0.0055 Torr vacuum, 2-cyclopentadienyl-2-hydroxypropane (4.0 g, 30.8 mmol) was heated to 90 °C and vaporized over a period of 2 h into a 350 °C Pyrex tube packed with glass beads. A yellow oil (3.2 g) was collected in a −190 °C trap. The crude product was loaded on a silica gel column. Eluting the column with pentane yielded a yellow solution. Removal of the pentane by distillation in a 55 °C oil bath afforded 0.32 g of dimethyl-6,6-d_6-fulvene (**7**).[19] ^{1}H NMR ($CDCl_3$): δ 6.49 (m, 2 H), 6.55 (m, 2 H). ^{2}H NMR ($CHCl_3$): δ 2.15 (br s). ^{13}C NMR ($CDCl_3$) δ 22.1 (septet, J = 19 Hz), 120.6 (d, J = 168 Hz), 130.7 (d, J = 168 Hz), 142.6 (s), 150.2 (s). MS *m/z* (relative intensity) 112 (M$^+$, 100), 94 (87). The labeled methyl groups contain 95% deuterium based on mass spectroscopic analysis in which d_6:d_5:d_4 = 100:9:15.

Eluting the column with 30% ethyl acetate in hexanes yielded 2.45 g of the starting alcohols.

6-(Methyl-d_3)-6-methylfulvene (8). Freshly distilled cyclopentadiene (1.50 g, 22.7 mmol) was dissolved in 15 mL of THF and cooled to −41 °C in an acetonitrile−liquid nitrogen bath. *n*-BuLi (1.6 M in ether, 11.0 mL, 17.6 mmol) was added dropwise under an Ar atmosphere over 30 min. A white precipitate formed and then

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[22] DePuy, C. H. *Org. Mass Spectrom.* **1985**, *20*, 556−559.

[23] DePuy, C. H.; Doren, J. M. V.; Gronert, S.; Kass, S. R.; Motell, E. L.; Ellison, G. B.; Bierbaum, V. M. *J. Org. Chem.* **1989**, 1846−50.

[24] DePuy, C. H.; Kass, S. R.; Bean, G. P. *J. Org. Chem.* **1988**, *53*, 4427−4433.

[25] The same kind of reaction was observed with *m*-xylene radical anion to give the *m/z* = 134 adduct. TME$^{\bullet-}$ also reacts with NO$^\bullet$ free radical.

[26] *CRC Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC: Boca Raton, FL, 1992.

[27] Stirk, K. M.; Orlowski, J. C.; Leeck, D. T.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 8604−8606.

[28] Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800.

[29] Waters, W. L.; Rollin, A. J.; Bardwell, C. M.; Schneider, J. A.; Aanerud, T. W. *J. Org. Chem.* **1976**, *41*, 889−891.

disappeared upon stirring. A methylene chloride solution of acetone-*1,1,1-d_3* (containing 3.0 g of acetone-*1,1,1-d_3*, 49 mmol, 98% D) was added swiftly, and a bright yellow color developed immediately. After stirring for 3 min, the solution was poured into a mixture of 30 mL of ice water and 30 mL of pentane. The organic layer was separated and washed with six 15-mL portions of ice water until the aqueous layer was neutral. The organic layer was then washed with two 15-mL portions of brine, dried over $MgSO_4$, and filtered. Most of the solvent was removed by distillation through a 15-cm column packed with glass beads at atmospheric pressure. The residual yellow oil was transferred to a 10-mL round-bottom flask and distilled at 5 Torr and 61−62 °C, to yield 0.82 g (33%) of **8** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 2.21 (s, 3 H), 6.49 (m, 2 H), 6.53 (m, 2 H). ^{2}H NMR ($CHCl_3$, C_6F_6): δ 2.16 (s, 3 D), 6.53 (s, 0.1 D). ^{13}C NMR ($CDCl_3$) δ 22.6 (septet, J = 20 Hz), 23.1 (q, J = 127 Hz), 120.7 (d, J = 168 Hz), 130.7 (d, J = 153 Hz), 142.5 (s), 150.1 (s). MS *m/z* (relative intensity) 109 (M^+, 100), 94 (78), 91 (82). The labeled methyl group contains 92% deuterium based on mass spectroscopic analysis in which d_3:d_2:d_1:d_0 = 100:13:9:0.

The sample was subjected to bulb-to-bulb distillation and three freeze−pump−thaw cycles before being used in the flowing afterglow experiment.

Gas-Phase Reactions. The flowing afterglow apparatus (FA) used in these studies has been described previously.[30] Typically, 0.2 Torr of argon at a constant volumetric flow rate of ca. 64 STP cm^3 s^{-1} was used as the buffer gas. The atomic oxygen radical anion was produced by dissociative electron attachment to N_2O; the N_2O was introduced into the ion source region of the FA at a constant flow rate of less than 0.05 STP cm^3 s^{-1}. We find that using Ar as the buffer gas for the $O^{\bullet-}$ reactions leads to fewer experimental complications than He; less unwanted Penning ionization and substantially smaller contaminating HO^- signals are observed. Numerous comparisons indicate that the reactions are otherwise independent of whether He or Ar is used as the buffer gas. Rate coefficients were obtained by monitoring reactant ion concentrations under pseudo-first-order conditions, with a constant flow of neutral molecules added at different reaction distances.[31] The volumetric flow rates of the neutrals needed to determine the rate coefficients were obtained by timing a pressure rise in a calibrated volume. Branching ratios were obtained by monitoring all the important ion intensities as a function of reaction time and then fitting those data to an appropriate kinetic scheme using a custom-written simplex-based fitting program.[32]

Acknowledgment. We acknowledge generous support of this work by the National Science Foundation.

JA952358E

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[30] (a) Grabowski, J. J.; Melly, S. J. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 147−164. (b) Grabowski, J. J.; Guo, Y. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 297−326.

[31] Graul, S. T.; Squires, R. R. *Mass Spectrom. Rev.* **1988**, *7*, 263−358.

[32] This program is designed for the reactions that give more than one product ion. Under the pseudo-first-order reaction conditions, competing and multistage reaction paths are simulated using the data from branching ratio measurements and various border conditions to single out the primary ion product(s) and create a scheme for complex reactions.