119 yields the final product of the dehydration reaction. The same is true for the ion of m/z 87 (Table II): at low excitation energies, this ion yields an abundant fragment ion of m/z 59 which further decomposes by loss of water to yield an ion of m/z 41 (a small amount of an ion of m/z 43 is also obtained at very high excitation energies). These findings suggest that some of the intermediates c are generated with an insufficient amount of energy for further reaction but that the reaction can be induced by collisional activation. Reaction of $CH_3O{-}^{10}B^+{-}OCH_3$ with diethyl ether yields an intermediate ion of m/z 118 instead of m/z 119. This demonstrates that the proposed intermediate contains boron. Further, reaction of $CH_3O{-}^{11}B^+{-}OCH_3$ with d_{10}-diethyl ether yields an ion corresponding to c with six deuterium atoms (m/z 125; Figure 3). Thus, all the hydrogen atoms in the first eliminated ethylene must originate from the ether. Finally, an ion corresponding to the intermediate c must be generated upon collisions of $CH_3O{-}^{11}B^+{-}OCH_3$ with ethanol (Scheme II). This ion decomposes spontaneously by loss of ethylene (Table I) to yield the ions e and/or f shown in Scheme II.

Alcohols that cannot lose an alkene according to Scheme II are not dehydrated by the boron cations. For example, methanol does not undergo any apparent reaction with $CH_3O{-}B^+{-}OCH_3$. Further, ethers that cannot lose two alkenes according to Scheme I are not dehydrated. Only slow condensation[2a] is observed for anisole and tetrahydrofuran (Table I). n-Butyl methyl ether undergoes a facile reaction (efficiency 0.9) with $CH_3O{-}^{11}B^+{-}OCH_3$ to yield an ion corresponding to the intermediate c: $(CH_3O)_2B{-}O(H)CH_3^+$ (m/z 105). Collision-activated dissociation of this product ion (Table II) is in agreement with the structural assignment: loss of methanol dominates the fragmentation.

The reaction of $CH_3O{-}B^+{-}OCH_3$ with n-butyl methyl ether yielding $(CH_3O)_2B{-}O(H)CH_3^+$ and neutral butene is analogous to the first elimination step in Scheme I. In order to obtain an estimate for the enthalpy change associated with this reaction, the proton affinity of trimethyl borate was determined. Protonated trimethyl borate was allowed to react with n-propanol (proton affinity 190.8 kcal/mol[13]), *sec*-butanol (proton affinity 195.0 kcal/mol[13]), tetrahydropyran (proton affinity 199.7 kcal/mol[13]), and diethyl ether (proton affinity 200.2 kcal/mol[13]). Proton transfer was observed to occur only to tetrahydropyran and diethyl ether. This brackets the proton affinity of trimethyl borate between that of *sec*-butanol and tetrahydropyran (195.0–199.7 kcal/mol). Hence, the elimination of butene from n-butyl methyl ether by the ion $CH_3O{-}B^+{-}OCH_3$ is estimated[16] to be exothermic by at least 50 kcal/mol. For diethyl ether, the elimination of two ethylenes by $CH_3O{-}B^+{-}OCH_3$ is estimated to be exothermic by at least 40 kcal/mol.[16,17]

The hydrogen-bonded structures b and d, if they occur as distinct intermediates on the reaction path, are not likely to be long-lived (they may actually correspond to transition states). This is indicated by results obtained upon investigation of the bimolecular reactions of an ion of m/z 93 corresponding to either c or b with six deuteriums (i.e., $(CH_3)_2B{-}O(D)CD_2CD_3^+$; from the reaction of $CH_3{-}^{11}B^+{-}CH_3$ with d_{10}-diethyl ether). The ion of m/z 93 is unreactive toward neutral ethylene. A facile exchange of deuterated ethylene with undeuterated ethylene is expected to take place for this ion if it had the structure d. Thus, the covalently bound structure c is more likely for the long-lived ion of m/z 93.

Conclusions

The B–O bond is among the strongest of all chemical bonds. Formation of this bond is likely to be the driving force for the observed abstraction of a water molecule from dialkyl ethers by dicoordinated boron cations. Initial addition of an ether molecule to the boron cation is highly exothermic, and some of this energy is used to eliminate first one and then a second alkene from acyclic ethers with alkyl groups that can be eliminated as alkenes. The high reactivity of the ions studied explains, in part, the difficulty to study simple dicoordinated boron cations in organic solvents. In sharp contrast, analogous carbon and phosphorus ions, e.g., $CH_3O{-}CH{-}OCH_3^+$ and $CH_3O{-}P{-}OCH_3^+$, were found to be unreactive toward diethyl ether in the gas phase. We are currently investigating reactions of gaseous dicoordinated boron cations with a variety of other organic substrates.

Acknowledgment. Financial support provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-9107121) is gratefully acknowledged.

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(16) $(CH_3O)_3B$, $\Delta H_f = -215.7$ kcal/mol (ref 13); $CH_3(CH_2)_3OCH_3$; $\Delta H_f = -61.7$ kcal/mol (ref 13); $CH_3CH_2CH{=}CH_2$; $\Delta H_f = -0.1$ kcal/mol (ref 13); $CH_3O{-}B^+{-}OCH_3$, $\Delta H_f \simeq 66$ kcal/mol (AM1).

(17) $(CH_3O)_2BOH_2^+$, $\Delta H_f = -61$ kcal/mol, on the basis of $(CH_3O)_2B{-}OH$, $\Delta H_f = -251$ kcal/mol (estimated using Benson's method), proton affinity on OH 176 kcal/mol (proton affinity of $(HO)_3B$, ref 5); diethyl ether, $\Delta H_f = -60.1$ (ref 13); ethylene, $\Delta H_f = 12.5$ (ref 13).

The Identification of Distonic Radical Cations on the Basis of a Reaction with Dimethyl Disulfide

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Abstract: A novel bimolecular reaction selective for radical cations with spatially separated radical and charge sites (distonic ions) is reported. Gas-phase reactions of dimethyl disulfide with radical cations containing oxygen functionalities were studied in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer. Conventional radical cations (generated by removing an electron from a stable neutral molecule), as well as enol radical cations, undergo fast charge exchange with dimethyl disulfide. However, distonic radical cations abstract $CH_3S^\bullet$ from dimethyl disulfide (the reaction is often accompanied by charge exchange). Related even-electron cations are unreactive toward dimethyl disulfide. Hence, the observation of $CH_3S^\bullet$ abstraction is indicative of a distonic ion structure. This approach was used to identify two distonic ions formed in ion–molecule reactions involving other distonic ions. One of these product ions is a novel sulfur-containing distonic ion: $(CH_3)_2S^+{-}CH_2^\bullet$.

Introduction

Characterization of the structure of a gaseous radical cation is a difficult and time-consuming task. Various experimental strategies, usually based on a combination of different types of data, have been developed just for the determination of the connectivity of atoms in polyatomic ions.[1] The recognition of the stability[2] and generality[3] of *distonic ions*, ions with spatially

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(1) See, for example: (a) McLafferty, F. W. *Science* **1981**, *214*, 280. (b) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

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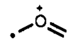
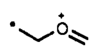
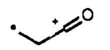
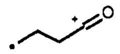
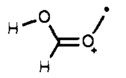
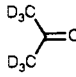
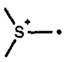
Table I. Reaction of Distonic Ions with Dimethyl Disulfide in the Gas Phase

					product ions			
ion	m/z	reference	k^a	$k_{ADO}{}^b$	m/z	%	reaction	ΔH^c
	44	9	2.1	2.2	61, 63	100	$CH_3S^\bullet$ abstraction, loss of CH_2O	−8
					91^d	trace	$CH_3S^\bullet$ abstraction	
	58	10	1.6	2.0	75^d	25	$CH_3S^\bullet$ abstraction, loss of CH_2O	
					94, 96	40	e^- transfer	-41^e
					105^d	35	$CH_3S^\bullet$ abstraction	
	56	11	1.6	2.1	94, 96	93	e^- transfer	-24^f
					103^d	7	$CH_3S^\bullet$ abstraction	
	70	3	1.1	1.9	94, 96	43	e^- transfer	-3^g
					117, 119	55	$CH_3S^\bullet$ abstraction	
	60	12	1.8	2.0	95, 97	100	H^+ transfer	−18
	78	9	0.5	1.9	94, 96	81	e^- transfer^e	-26^h
					125^d	19	$CH_3S^\bullet$ abstraction	
	76		0.1	1.9	123, 125	100	$CH_3S^\bullet$ abstraction	

[a] Reaction rate, in units of 10^{-9} cm^3 molecule^{-1} s^{-1}. [b] Collision rate, in units of 10^{-9} cm^3 molec^{-1} s^{-1}, see ref 7. [c] Given in kcal/mol; calculated using data given in ref 6. [d] The signal-to-noise ratio was not good enough to detect the ^{34}S isotope peak. [e] For the production of $CH_2{=}CH_2$ and $CH_2{=}O$; ref 11a. [f] For the production of $CH_2{=}CH_2$ and CO. [g] For the production of $CH_2{=}CH_2$ and $CH_2{=}C{=}O$. [h] Assuming that $CD_2{=}C(CD_3)OCDH_2{}^+$ is the reaction ion.

separated charge and radical sites, has created a need for new approaches of ion structure verification. For example, although the formation of distonic ions in dissociation and isomerization reactions of molecular ions is frequently proposed in the literature, the existence of stable distonic ions has been conclusively demonstrated in only a few cases.[3] We report here a novel bimolecular reaction that allows the positive identification of distonic radical cations.

Experimental Section

All the experiments were carried out in a dual-cell Extrel FTMS-2001 Fourier transform ion cyclotron resonance mass spectrometer[4,5] (FT-ICR) equipped with a superconducting magnet (2.5 T). The dual-cell consists of two cubic 2″ cells sharing a common wall (the conductance limit plate), and it is differentially pumped by two turbomolecular pumps. The base pressure in each side of the cell is less than 1 × 10^{-9} Torr, as indicated by an ionization gauge on each side.

The primary ions were generated by electron ionization in one side of the cell. In some instances, the primary ions were used to generate the ions of interest by ion–molecule reactions with neutral molecules added to the cell at about 1 × 10^{-7} Torr. The desired ions were transferred into the other side of the dual cell for examination of their reactions with dimethyl disulfide. Prior to the reactions, the ions were collisionally cooled by pulsing a relatively high pressure (about 1 × 10^{-5} Torr) of argon into the cell for a short time period (about 800 ms). After this, the desired ions were isolated by ejecting all the unwanted ions from the cell through the use of single frequency ejection pulses and frequency sweeps. The ions were then allowed to react with dimethyl disulfide (about 1 × 10^{-7} Torr) for variable periods of time.

For rate measurements, the ion gauges were calibrated by measuring apparent rates for reactions with known rate constants, as described earlier.[4,5] Precision of the rate measurements is better than ±5%; the accuracy is estimated to be better than ±50%. All the reagents were obtained commercially and used as received. The samples were introduced into the FT-ICR through an Extrel manufactured, heated batch inlet system equipped with a leak valve.

Results and Discussion

It was recently demonstrated[4] in our laboratory that ionization of cyclobutanone in the gas phase yields a stable γ-distonic ion: $^\bullet CH_2CH_2CH_2C^+{=}O$. The ion was found to undergo a variety of interesting bimolecular reactions, many of which entail homolytic bond cleavages. One of these reactions involves the abstraction of $CH_3S^\bullet$ from dimethyl disulfide. This novel reaction has no well-known precedent in the gas phase or in solution. Hence, we decided to investigate the generality of this reaction by using a number of conventional and distonic radical cations, most of them with oxygen functionalities.

Conventional radical cations do *not* abstract $CH_3S^\bullet$ from CH_3SSCH_3. Exothermic[6] charge exchange occurs at every collision for all the conventional radical cations studied thus far,[7] and it is the only reaction observed. The ions studied include the molecular ions of simple organic ethers (e.g., ethyl vinyl ether, oxetane), ketones (e.g., acetone, cyclopentanone, cyclohexanone), lactones (γ-butyrolactone, δ-valerolactone), and alkenes (2-hexene). Enol radical cations, such as the ions $CH_2{=}C(OH)_2{}^{\bullet+}$ and $CH_2{=}C(OH)OCH_3{}^{\bullet+}$,[8] also show only electron transfer with CH_3SSCH_3.

Strikingly different results were obtained when distonic ions with well-characterized[3,9–12] structures were studied (the first five entries in Table I): *abstraction of $CH_3S^\bullet$ was found to be common for these distonic ions containing oxygen functionalities.* The reaction is often accompanied by dissociative[10a,13] charge exchange.

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(2) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225.

(3) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123.

(4) Stirk, K. G.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1991**, *113*, 5880.

(5) Zeller, L.; Farrell, J., Jr.; Vainiotalo, P.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 1205.

(6) 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)

(7) For calculation of collision rates, see: (a) Chesnavich, W. J.; Su, T.; Bowers, M. T. *J. Chem. Phys.* **1980**, *72*, 2641. (b) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183. (c) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.

(8) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 1591.

(9) (a) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724. (b) Blair, A. B.; Harrison, A. G. *Can. J. Chem.* **1973**, *51*, 703. (c) Bouma, W. J.; MacLeod, J. K.; Radom, L. *Adv. Mass Spectrom.* **1979**, *8A*, 178.

(10) (a) Wittneben, D.; Grützmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 545. (b) Baumann, B. C.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 7927. (c) Kiminkinen, L. K. M.; Stirk, K.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 2027.

(11) Traeger, J. C.; Hudson, C. E.; McAdoo, D. J. *Org. Mass Spectrom.* **1989**, *24*, 230.

(12) (a) Wesdemiotis, C.; Feng, F.; Williams, F. *Org. Mass Spectrom.* **1986**, *21*, 689. (b) Villeneuve, S.; Burgers, P. C. *Prog. Mass Spectrom.* **1986**, *21*, 733. (c) Stirk, M. K.; Kiminkinen, L. M.; Kenttämaa, H. I. *Chem. Rev.*, in press. (d) Leeck, D. T.; Zeller, L.; Stirk, K. G.; Kiminkinen, L. M.; Castro, L.; Vainiotalo, P.; Kenttämaa, H. I. Manuscript in preparation.

(13) Charge transfer without accompanying dissociation would be endothermic.

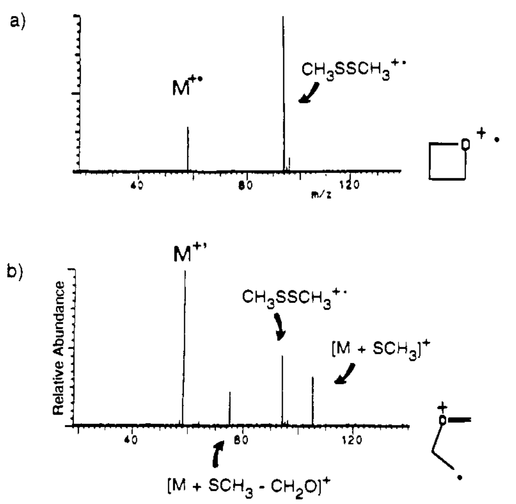
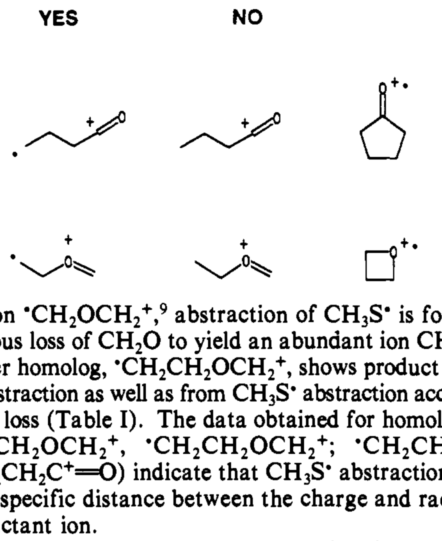


Figure 1. (a) Reaction of ionized oxetane with dimethyl disulfide. (b) Reaction of the distonic isomer, $^{\bullet}CH_2CH_2OCH_2{}^+$, with dimethyl disulfide. The reaction time was 300 ms, and the dimethyl disulfide pressure was 1×10^{-7} Torr for both experiments.

Chart I. $CH_3S^{\bullet}$ Abstraction from CH_3S–SCH_3



For the ion $^{\bullet}CH_2OCH_2{}^+$,[9] abstraction of $CH_3S^{\bullet}$ is followed by spontaneous loss of CH_2O to yield an abundant ion $CH_3SCH_2{}^+$. The higher homolog, $^{\bullet}CH_2CH_2OCH_2{}^+$, shows product ions from $CH_3S^{\bullet}$ abstraction as well as from $CH_3S^{\bullet}$ abstraction accompanied by CH_2O loss (Table I). The data obtained for homologous ion pairs ($^{\bullet}CH_2OCH_2{}^+$, $^{\bullet}CH_2CH_2OCH_2{}^+$; $^{\bullet}CH_2CH_2C^+{=}O$, $^{\bullet}CH_2CH_2CH_2C^+{=}O$) indicate that $CH_3S^{\bullet}$ abstraction does not require a specific distance between the charge and radical sites in the reactant ion.

The only distonic ion shown in Table I that does *not* abstract $CH_3S^{\bullet}$ from dimethyl disulfide is $HC^+(OH)OCH_2{}^{\bullet}$.[12] This ion is a very strong Brönsted acid. Hence, it is not surprising that proton transfer was found to be the only reaction for this ion: proton transfer often dominates over all other reaction channels for gas-phase ions if it is exothermic. It is concluded that the absence of $CH_3S^{\bullet}$ abstraction, especially if a fast proton transfer is observed, does not allow one to *rule out* a distonic structure for the reacting ion. $CH_3S^{\bullet}$ abstraction may be expected only for those distonic ions whose conjugate base has a proton affinity lower than that of CH_3SSCH_3 (196 kcal/mol[6]). However, it is clear from Table I that the $CH_3S^{\bullet}$ abstraction channel can successfully compete with highly exothermic charge exchange (e.g., see the reaction of $^{\bullet}CH_2CH_2OCH_2{}^+$).

Even-electron ions were found to be unreactive toward CH_3SSCH_3. This is true, for example, for $CH_3CH_2CH_2C^+{=}O$ and $CH_3CH_2OCH_2{}^+$ which are the even-electron analogs of $^{\bullet}CH_2CH_2CH_2C^+{=}O$ and $^{\bullet}CH_2CH_2OCH_2{}^+$, respectively. This finding, together with the fact that various distonic radical cations abstract $CH_3S^{\bullet}$ from CH_3SSCH_3 while the isomeric (Figure 1) or related conventional radical cations (see Chart I) react only by charge exchange, strongly suggests that the prerequisite for $CH_3S^{\bullet}$ abstraction is the presence of a radical site remote from the charge site in the reactant ion. Hence, the reaction is likely to involve C–S bond formation at the radical site of the ion. The mechanism of this interesting reaction is under investigation. However, all the evidence currently available[14] supports the expectation that the $CH_3S^{\bullet}$ abstraction reaction will occur for most distonic radical cations with the odd spin on a carbon center.

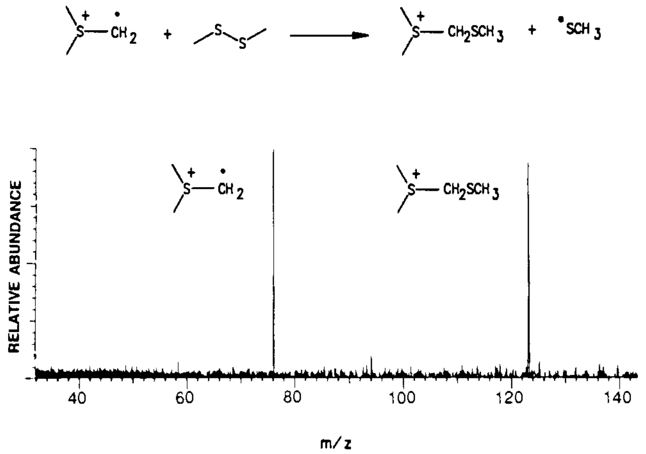


Figure 2. Reaction of dimethyl disulfide (1.2×10^{-7} Torr) with the ion of *m/z* 76 generated by transferring $CH_2{}^{\bullet +}$ from $^{\bullet}CH_2CH_2CH_2CO^+$ to CH_3SCH_3. The reaction time was 7 s.

Finally, CH_3SSCH_3 was used to examine whether the radical cations generated in ion–molecule reactions of two different distonic ions have distonic structures themselves. The well-documented[9] transfer of $CH_2{}^{\bullet +}$ from $^{\bullet}CH_2OCH_2{}^+$ to d_6-acetone[15] yields an ion that is likely to have the distonic structure $(CD_3)_2C^+$–$OCH_2{}^{\bullet}$. The ion was observed to abstract $CH_3S^{\bullet}$ from CH_3SSCH_3 (Table I). Charge exchange is also observed; the slow rate of this reaction precludes the possibility that the reactant ion had a conventional structure, such as $CD_2{=}C(CD_3)OCH_2D^{\bullet +}$. A linear decay of the reactant ion as a function of time indicates that the ion does not have a mixture of structures. All these observations suggest that the ion has retained the original distonic structure, and that the observed slow charge exchange reaction occurs via isomerization of the ion within the collision complex with dimethyl disulfide.

Another, different radical cation (*m/z* 76) is generated by $CH_2{}^{\bullet +}$ transfer to CH_3SCH_3 from $^{\bullet}CH_2CH_2CH_2C^+{=}O$ (through loss of $CH_2{=}CH_2$ and CO) or $^{\bullet}CH_2OCH_2{}^+$ (through loss of CH_2O). The product ion reacts with dimethyl disulfide by exclusive $CH_3S^{\bullet}$ abstraction (Figure 2). It is concluded that the ion has a distonic structure, most likely $(CH_3)_2S^+$–$CH_2{}^{\bullet}$. Note that simple sulfur-containing distonic ions are predicted to be less stable than their conventional isomers,[2b] and that only one other gaseous, sulfur-containing distonic ion has been reported[3] before.

Acknowledgment. The National Science Foundation (CHE-9107121), the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the Grace Corporation, are thanked for financial support.

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(14) Besides $H\dot{C}^+(OH)OCH_2{}^{\bullet}$, we have only encountered one other distonic ion, the ion $(CH_3O)_3P^+$–$OCH_2CH_2{}^{\bullet}$ (see ref 10c), that has been conclusively shown to have a distonic structure but that does not react with dimethyl disulfide by $CH_3S^{\bullet}$ abstraction. This ion was found to be remarkably unreactive toward many neutral reagents for reasons that are not clear at this time.

(15) d_6-Acetone was used instead of acetone since the undeuterated distonic ion would have a *m/z* value close to an abundant fragment ion of 1,3-dioxolane, the source of $^{\bullet}CH_2OCH_2{}^+$.