

Novel [3 + 2] 1,3-Cycloaddition of the Ionized Carbonyl Ylide $^+\text{CH}_2\text{OCH}_2^\bullet$ with Carbonyl Compounds in the Gas Phase

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Abstract: For the first time [3 + 2] 1,3-cycloaddition of an ionized carbonyl ylide has been observed in gas phase ion–molecule reactions of $^+\text{CH}_2\text{OCH}_2^\bullet$ (**1**) with several carbonyl compounds. The reaction, which competes with electrophilic addition that leads to net $\text{CH}_2^{+\bullet}$ transfer, occurs across the C=O double bond of acetaldehyde and several acyclic ketones yielding ionized 4,4-dialkyl-1,3-dioxolanes as unstable cycloadducts. Rapid dissociation of the nascent cycloadducts by loss of a 4-alkyl substituent as a radical leads to the observed products, that is cyclic 4-alkyl-1,3-dioxolanylium ions. Cycloaddition of **1** with cyclic ketones yields bicyclic spiro adducts, which also undergo rapid dissociation. Cyclobutanone yields ionized 1,3-dioxaspiro[4,3]octane, which dissociates exclusively by neutral ethene loss to ionized 4-methylene-1,3-dioxolane. Ionized 1,3-dioxaspiro[4,4]nonane is formed in reactions with cyclopentanone, and its rapid dissociation by loss of C_3H_6 and $\text{C}_2\text{H}_5^\bullet$ yields the ionized 4-methylene-1,3-dioxolanylium and the 4-ethenyl-1,3-dioxolanylium product ions, respectively. A systematic study of this novel reaction and characterization of the product ions carried out *via* pentaquadrupole (QqQqQ) multiple stage (MS^2 and MS^3) mass spectrometric experiments provide experimental evidence for the cycloaddition mechanism. The dissociation chemistry observed for the cycloaddition products correlate well with their proposed structures and was compared to that of both isomeric and reference ions. *Ab initio* MP2/6-31G(d,p)//HF/6-31G(d,p) + ZPE potential energy surface diagrams for the reactions of **1** with acetone, fluoroacetone, and 1,1,1-trifluoroacetone support the operation of the two competitive reaction pathways, that is $\text{CH}_2^{+\bullet}$ transfer and [3 + 2] 1,3-cycloaddition/dissociation, and show that the cycloaddition process is favored by electron-withdrawing substituents.

Introduction

Cycloadditions, that is reactions in which two unsaturated molecules combine to form a cyclic product, are remarkably important in condensed phase chemistry, being one of the most useful reactions in synthesis.¹ Although these reactions most often employ uncharged or dipolar components, many even-electron negatively (M^-) and positively charged (M^+) species generated in solution also participate in a number of synthetically useful reactions known as polar cycloadditions.^{2,3} Odd-electron cations ($\text{M}^{+\bullet}$) also undergo efficient “hole”-catalyzed polar cycloadditions in solution,^{4,5} which often display contrasting reactivity and improved yields as compared to the corresponding reactions involving their neutral counterparts.

In the gas phase, the occurrence of a few cycloaddition reactions of even-electron cations has been sporadically proposed.⁶ Recently⁷ a systematic study has demonstrated the occurrence of unprecedented polar [4 + 2⁺] cycloadditions of acylium ions ($\text{RC}^+=\text{O}$) with several “s-cis” conjugated dienes.^{7a,b}

Similar gas phase polar [4 + 2⁺] cycloadditions also have been recently observed for nitrilium ($\text{RC}\equiv\text{N}^+\text{R}$),^{7c} immonium ($\text{RRC}=\text{N}^+\text{RR}$),^{7c} sulfonium ($\text{RRC}=\text{S}^+\text{R}$),^{7d} and the phenyl sulfinyl cation ($\text{PhS}^+=\text{O}$).^{7e} Cycloadditions of odd-electron cations, on the other hand, have been long observed and extensively investigated in the gas phase.^{5,8} Contrasting reactivity and significant changes in product yields have been often observed as compared to the corresponding neutral reactions in solution.

In the condensed phase, 1,3-dipolar compounds such as ylides of nitriles and azomethines participate in [4 + 2] cycloadditions that are known specifically as 1,3-dipolar cycloadditions.⁹ Carbonyl ylides (see general structure below), regardless of their relative instability, are also useful 1,3-dipoles in 1,3-dipolar

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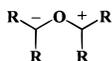
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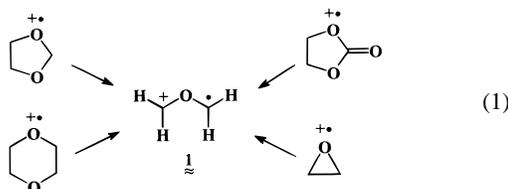
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cycloadditions.^{9,11} They participate as elusive intermediates in thermal and photochemical decomposition of epoxides,¹⁰ diazoketones,^{11a} oxadiazolines,^{11b} and oxethanones^{11c} and have been efficiently trapped with several dipolarophiles by 1,3-dipolar cycloadditions. The simplest carbonyl ylide $^+\text{CH}_2\text{OCH}_2^-$ is, however, an unknown species, and its possible but apparently unfavorable formation from ring opening of neutral ethylene oxide has been theoretically investigated.¹⁰



Cycloadditions involving ionized 1,3-dipoles are unprecedented both in the condensed and gas phase. However, a variety of these so-called α -distonic ions¹² can be efficiently generated in the gas phase via several MS techniques. Whereas their neutral counterparts are often unstable species, ionized 1,3-dipoles show relatively high gas phase kinetic and thermodynamic stability as demonstrated both experimentally¹² and theoretically.¹³ Therefore, the ability of ionized 1,3-dipoles to undergo [3 + 2] 1,3-cycloadditions¹⁴ in the gas phase could be investigated. The *stable*¹⁵ ionized form (**1**) of the simplest, yet unknown and probably unstable¹⁰ carbonyl ylide $^-\text{CH}_2\text{OCH}_2^+$, can be readily generated in the gas phase (eq 1) either by dissociative ionization of 1,3-dioxolane,^{15a} 1,4-dioxane,^{15b} and ethylene carbonate^{15c} or by ionization followed by rapid C–C ring-opening of ethylene oxide.¹⁶



In the present study,¹⁷ the gas phase ion–molecule chemistry of $^+\text{CH}_2\text{OCH}_2^+$ (**1**) with several carbonyl compounds has been systematically investigated via multiple stage (MS² and MS³) pentaquadrupole (QqQqQ) mass spectrometry.¹⁸ [3 + 2] 1,3-cycloaddition has been established as a major reaction pathway, a process that is supported both experimentally and theoretically

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(14) Cycloaddition reactions are classified in terms of the number of π electrons of each component participating in the reaction. Thus, cycloaddition reactions of **1** ($^+\text{CH}_2\text{OCH}_2^+$), a 3π electron and a 1,3-coupling species, with 2π electron species are termed [3 + 2] 1,3-cycloaddition.

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via *ab initio* calculations. The first example of cycloaddition involving an ionized carbonyl ylide is therefore reported.

Experimental and Theoretical Methods

The experiments were performed using a high transmission Extrel [Pittsburgh, PA] pentaquadrupole mass spectrometer, which has been described in detail elsewhere.^{18e} The instrument consists basically of three mass analyzing (Q1, Q3, Q5) and two reaction (q2, q4) quadrupoles. Ion **1** was generated by 70 eV dissociative electron ionization (EI) of 1,3-dioxolane.^{15a} Ion–molecule reactions of **1** were performed by MS² experiments in which **1** was mass-selected by Q1 and then reacted at near zero eV collision energy with the neutral reagent introduced in q2. The corresponding product spectrum was acquired by scanning Q5, while Q3 and q4 were operated in the “full-transmission” rf-only mode. For the MS³ experiments,¹⁹ one of the ion–molecule products of interest generated in q2 was mass selected in Q3 and 15 eV collisions with argon were performed in q4, while Q5 was scanned to record the spectrum. The collision energies were calculated as the voltage difference between the ion source and the reaction quadrupole. The total pressures inside each differentially pumped region, which were determined to correspond to multiple collision conditions¹⁸ in both q2 and q4, were typically 2×10^{-6} (ion-source), 8×10^{-6} (q2), and 6×10^{-5} (q4) Torr, respectively.

Ab initio calculations were carried out by using Gaussian94.²⁰ The open and closed shell cations were optimized at the unrestricted (UHF) or restricted (RHF) Hartree-Fock level of theory, respectively, and by employing the polarization 6-31G(d,p) basis set.²¹ Improved energies were obtained by using single point calculations at the 6-31G(d,p) level of theory and by incorporating valence electron correlations calculated by second-order Møller–Plesset (MP2) perturbation theory.²² Harmonic vibrational frequencies were calculated at the HF/6-31G(d,p) level in order to characterize the stationary points and to obtain the zero-point vibrational energies (ZPE).

4-Methyl-4-phenyl-1,3-dioxolane was obtained by the reaction of formaldehyde with (\pm)-2-phenyl-1,2-propanediol carried out according to an adapted procedure.²³ The following reference ions were obtained by either direct or dissociative 70 eV EI of acetaldehyde (**2**),²⁴ pyruvic acid (**3**),²⁵ butyraldehyde (**4**),²⁴ 4-methyl-4-phenyl-1,3-dioxolane (**8d**),²⁶ 2-ethyl-2-methyl-1,3-dioxolane (**11a**),²⁷ and 1,4-dioxaspiro[4,5]decane (**11c**).²⁷ Ion

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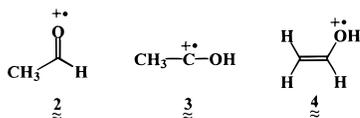
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11b was obtained by transacetalization²⁸ of 2-methyl-1,3-dioxolane with PhCO^+ , which was generated via 70 eV dissociative EI of acetophenone.

Results and Discussion

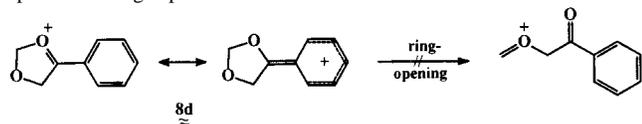
Structure²⁹ of the Reactant Ion. Several studies^{12c-e,15} have shown that dissociative EI of 1,3-dioxolane forms **1** as the primary $\text{C}_2\text{H}_4\text{O}^{+\bullet}$ fragment and that **1** efficiently transfers ionized methylene ($\text{CH}_2^{+\bullet}$) to a series of neutral compounds such as nitriles, ketones and pyridines.^{15,30} Theoretical calculations on $\text{C}_2\text{H}_4\text{O}^{+\bullet}$ isomers³¹ show, however, that **1** is less thermodynamically stable than its isomers **2**, **3**, and **4** (see structures below), hence occurrence for the primary **1** of isomerizations induced by collisions is a possibility that should be investigated under the present low energy quadrupole multiple collision conditions.



Extensive $\text{CH}_2^{+\bullet}$ transfer (m/z 55) is observed when the ion of m/z 44 produced from 70 eV dissociative EI of 1,3-dioxolane is mass-selected and then reacted with acetonitrile in q2 (Figure 1a). On the contrary, reactions with isomers **2** (Figure 1b), **3**, and **4** performed under identical experimental conditions produce mainly protonated acetonitrile of m/z 42 (and the proton-bound dimer of m/z 83). The reactant ions **2–4** also dissociates to a moderate extent by loss of a hydrogen atom (m/z 43). These results unequivocally demonstrate that **1** preserves its primary structure,²⁹ being kinetically stable under the present reaction conditions toward both isomerization and dissociation.

Reactions with Carbonyl Compounds. $\text{CH}_2^{+\bullet}$ Transfer. Reactions of **1** with acetone have been studied earlier, and $\text{CH}_2^{+\bullet}$ transfer was a main process observed.^{12c-e,15a} Under the present experimental conditions, **1** transfers $\text{CH}_2^{+\bullet}$ to all carbonyl compounds investigated to variable extents (Table 1 and Figures 2–3). Although several alternative structures are possible, structurally specific ion–molecule reactions³² have shown that the distonic ion $(\text{CH}_3)_2\text{C}=\text{O}^+\text{CH}_2^\bullet$ of m/z 72 is formed in $\text{CH}_2^{+\bullet}$ transfer to acetone (Figure 2a). Similar primary products (**6**,

(26) The cyclic ion **8d** is expected to be the primary ion formed upon dissociation by loss of a methyl radical of ionized 4-methyl-4-phenyl-1,3-dioxolane. Additionally, *ab initio* calculations at the MP2/6-31G(d,p)//HF/6-31G(d,p) level show that **8d** is 31.7 kcal/mol more stable than the acyclic isomer shown below, which is likely a result of charge delocalization in **8d** through the aromatic phenyl ring. This indicates that **8d** is a quite stable species in the gas phase.



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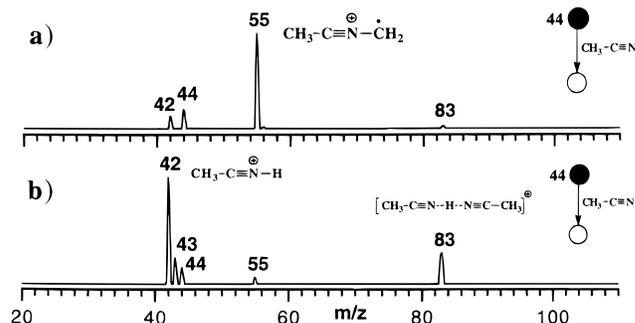
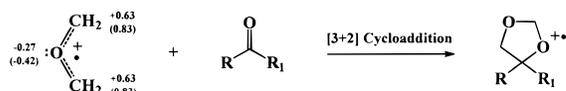
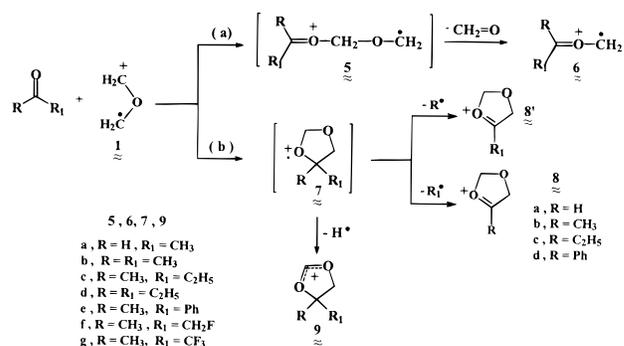


Figure 1. Double-stage (MS^2) product spectrum for ion–molecule reactions of the isomeric ions (a) **1** and (b) **2** with acetonitrile. The spectra of the isomers **3** and **4** are nearly identical to that of **2** (Figure b) and are not shown. Note that **1** reacts extensively by net $\text{CH}_2^{+\bullet}$ transfer (m/z 55), whereas protonated acetonitrile of m/z 42 and its proton bound dimer of m/z 83 are the main products for **2**, **3**, and **4**. In the terminology used to describe the type of experiment and scan mode employed, a filled circle represents a fixed (or selected) mass; an open circle, a variable (or scanned) mass, whereas the neutral reagent or collision gas that causes the mass transitions are shown between the circles. For more details on this nomenclature see ref 19.

Scheme 1



Scheme 2



see Scheme 2) are therefore expected for the other homologous ketones, although further isomerization may occur. Net CH^+ transfer is also observed for cyclopentanone (m/z 97, Figure 3b) and acetophenone (m/z 133, Table 1).

[3 + 2] 1,3-Cycloaddition.¹⁴ The data presented in Table 1 and Figures 2 and 3 show that other ionic products, in addition to the $\text{CH}_2^{+\bullet}$ (and CH^+) transfer products just discussed, are formed in reactions of **1** with carbonyl compounds. As shown in Scheme 1, both the positive charge and unpaired-electron of **1** are delocalized, with the charge and spin densities (in parenthesis) concentrated mainly and evenly on the two methylene groups.^{30b} This interesting electronic structure indicates that **1** may react at both of the CH_2 sites. Thus, [3 + 2] 1,3-cycloadditions comparable to those observed in condensed phase for larger neutral carbonyl ylides are possible (Scheme 1) and may explain the formation of the additional products.

The overall reactivity of **1** with carbonyl compounds (Scheme 2) could then involve a competition between electrophilic addition to the carbonyl oxygen (pathway a) and [3 + 2] 1,3-cycloaddition (pathway b),³³ which would yield for the *acyclic carbonyl*

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Table 1. Double-Stage Product Spectra for Ion–Molecule Reactions of **1** with Several Neutral Carbonyl Compounds^a

neutral reactant	products <i>m/z</i> (relative abundance)				
	protonated ^b reagent	CH ₂ ^{•+} transfer	CH ⁺ transfer	[3 + 2] 1,3-cycloaddition ^c	other products
acetaldehyde	45(62)	58(32)		87(100) ^d	89(18) ^e
acetone- <i>d</i> ₆	65(48)	78(100)		90(32)	129(16) ^e
fluoroacetone	77(56)	90(100)		87(99)	43(21)
2-butanone	73(5)	86(100)		87(94), 101(2)	71(4)
3-pentanone	87(5)	100(52)		101(100)	45(6), 173(13) ^e
acetophenone	121(8)	134(13)	133(100)	149(55)	119(3), 73(11)

^a Some spectra are shown as figures, see text. ^b Due to the multiple collision conditions, proton transfer may occur from either the reactant ion or its ion–molecule products. ^c Product ions **8** assigned as fragments of the intact cycloadducts **7** (see text). ^d Most likely a mixture of **8a** and the 4-methyl-1,3-dioxolanylium ion analogue of ions **11**. ^e The secondary proton transfer product, that is the corresponding proton bound dimer.

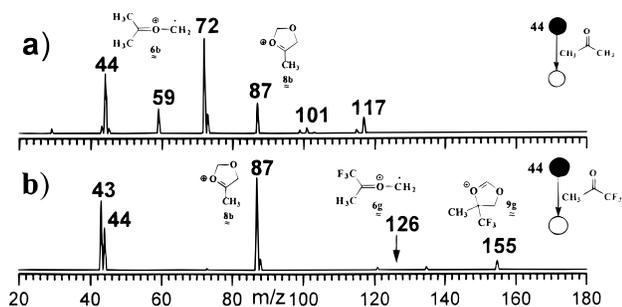


Figure 2. Double-stage product spectrum for ion–molecule reactions of **1** (*m/z* 44) with (a) acetone and (b) 1,1,1-trifluoroacetone. Note the dominance for 1,1,1-trifluoroacetone of the [3 + 2] 1,3-cycloaddition/dissociation products of *m/z* 87 and *m/z* 155, whereas acetone reacts mainly by net CH₂^{•+} transfer (*m/z* 72) and moderately by the cycloaddition/dissociation pathway (*m/z* 87).

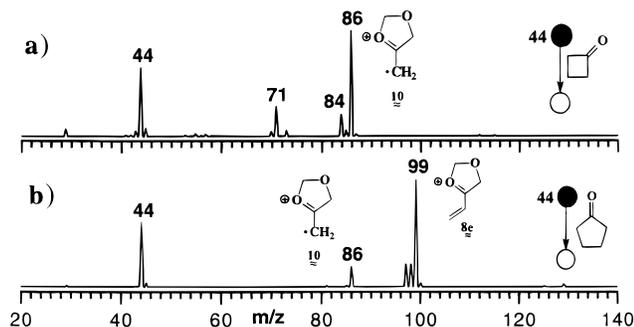


Figure 3. Double-stage product spectrum for ion–molecule reactions of **1** (*m/z* 44) with (a) cyclobutanone and (b) cyclopentanone. Two [3 + 2] 1,3-cycloaddition/dissociation products are observed for cyclopentanone (*m/z* 86 and *m/z* 99), whereas a single product (*m/z* 86) of this reaction pathway is seen for cyclobutanone.

compounds the ionized 4,4-dialkyl-1,3-dioxolane cycloadducts **7**. The two observed products, that is the CH₂^{•+} transfer products **6** and the cyclic 1,3-dioxolanylium ions **8**, would then be formed by rapid dissociation of both nascent adducts by loss of formaldehyde and an alkyl radical, respectively.

When these two competitive reaction pathways are assumed, all the products observed are easily rationalized. In regard to the cycloaddition/dissociation pathway, it is expected that the putative acetaldehyde cycloadduct (**7a**) loses a methyl radical (**8a**, *m/z* 73) and mainly a hydrogen atom (**8b**, *m/z* 87);³⁴ the acetone cycloadduct (**7b**) a methyl radical (**8b**, *m/z* 87);³⁵ the 2-butanone cycloadduct (**7c**) both an ethyl (**8b**, *m/z* 87) and a

(33) Little variation of the relative yields of products **6** and **8** were observed when varying significantly the collision pressure inside the reaction chamber (q2), which strongly suggested that **8** (and **6**) are primary products for reactions between **1** and the neutral carbonyl compound.

(34) Preferential loss of a hydrogen atom for **7a** is also observed during 70 eV dissociative ionization of 4-methyl-1,3-dioxolane. The mass spectrum²⁴ shows a fragment of *m/z* 87 (hydrogen atom loss) which is approximately six times as abundant as that of *m/z* 73 (methyl loss).

methyl radical (**8c**, *m/z* 101); the 3-pentanone cycloadduct (**7d**) an ethyl radical (**8c**, *m/z* 101); and the cycloadduct of acetophenone (**7e**) a methyl radical (**8d**, *m/z* 149),³⁶ whereas the cycloadducts of fluoroacetone (**7f**) and 1,1,1-trifluoroacetone (**7g**) should eliminate preferentially the fluorinated groups as radicals³⁷ to form **8b** of *m/z* 87. With no exception, ionic products of these expected *m/z* ratios are observed in the corresponding product spectra (Table 1 and Figure 2). Loss from **7b** of a methyl group supplied by acetone is confirmed when reacting acetone-*d*₆ (Table 1), for which a 3u mass shift (*m/z* 90) for the putative cycloaddition product (**8b-d₃) is observed. Low abundance fragments of *m/z* 101 (Figure 2a) and *m/z* 155 (Figure 2b) are also observed for **7b** and **7f**, respectively, a dissociation process that most likely occurs by elimination of one of their C2-hydrogens to form the corresponding resonance stabilized 1,3-dioxolanylium ions **9b,f** (Scheme 2).**

Evidence that firmly corroborates the competitive electrophilic addition/cycloaddition mechanism proposed in Scheme 2 is provided by the very contrasting and consistent reactivity displayed by acetone, fluoroacetone, and 1,1,1-trifluoroacetone. The strong electron withdrawing fluorine atom should diminish the nucleophilicity of the carbonyl oxygen of fluoroketones and consequently disfavor pathway (a) that leads to net CH₂^{•+} transfer. On the other hand, it is known that electron-withdrawing substituents on carbonyl compounds often enhance considerably the yields of their cycloaddition products, most likely by favoring frontier orbital interactions.³⁸ This trend is clearly reflected in the product spectra of acetone and the two fluoroacetones. Acetone (Figure 2a) reacts mainly by electrophilic addition that leads to net CH₂^{•+} transfer (*m/z* 72) and moderately by cycloaddition (*m/z* 87); fluoroacetone (Table 1) reacts by CH₂^{•+} transfer (*m/z* 90) and cycloaddition (*m/z* 87) to similar extents, whereas 1,1,1-trifluoroacetone (Figure 2b) reacts predominantly by cycloaddition (*m/z* 87 and 155).

The very characteristic reactivity displayed by two cyclic ketones (Figure 3) also provides evidence for the operation of a similar [3 + 2] 1,3-cycloaddition/dissociation mechanism

(35) A product ion of *m/z* 87 was also observed in the pioneering work of Blair and Harrison [Blair, A. S.; Harrison, A. G. *Can. J. Chem.* **1973**, *51*, 703] on reactions between acetone and oxirane both in their neutral and ionized forms. This ion was assigned mainly to the product of the following acetylation reaction: (CH₃)₂CO⁺ + C₂H₄O → C₂H₄O·COCH₃⁺ (*m/z* 87) + CH₃[•]. Considering that this reaction is not possible under the present mass-selected ion–molecule reaction conditions, there exists therefore the possibility that a similar product (**8b**, see Scheme 2) was formed by the reaction of ionized oxirane (i.e., **1**) and neutral acetone.

(36) The mass spectrum of 4-methyl-4-phenyl-1,3-dioxolane shows that **7e** dissociates extensively by loss of a methyl radical to form the most abundant fragment of *m/z* 149. No fragment of *m/z* 87 (loss of a phenyl radical) is observed.

(37) Preferential loss of CF₃[•] (not CH₃[•]) from **7g** is expected when examining, for instance, the mass spectrum of CF₃COCH₃, and noting the dominance of the CH₃CO⁺ fragment.

(38) (a) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976.

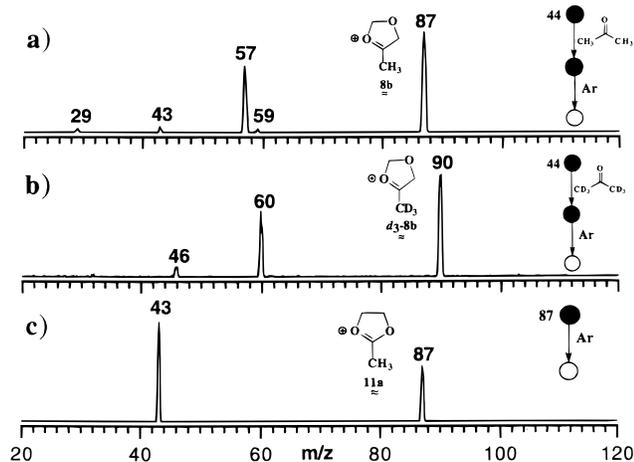
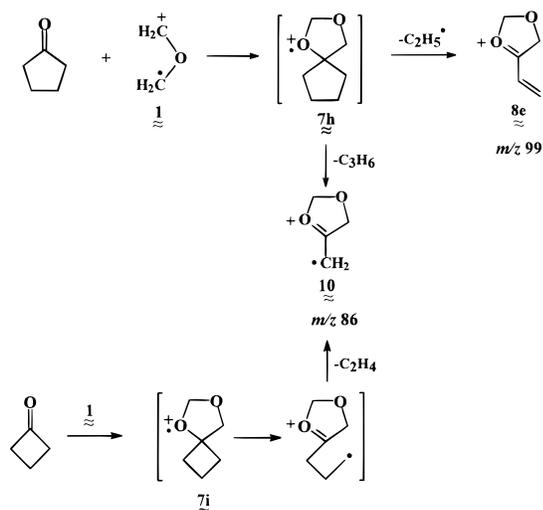


Figure 4. Triple-stage (MS^3) sequential product spectrum of (a) the m/z 87 (**8b**) and (b) m/z 90 (**8b-d₃**) products formed in ion–molecule reactions of **1** with acetone and acetone- d_6 , respectively, and (c) the double-stage dissociation spectrum of the isomeric **11a**. Ion **8b** eliminates mainly formaldehyde (m/z 57), whereas loss of C_2H_4O (m/z 43) dominates for **11a**.

Scheme 3



(Scheme 3). The bicyclic spiro 1,3-dioxaspiro[4,4]nonane ion **7h** and its [4,3]-analogue **7i** are the primary cycloaddition products expected in these cases. As for the isomeric 1,4-dioxaspiro[4,4]nonane ion,²⁷ **7h** is expected to fragment mainly to **8e** (m/z 99) and **10** (m/z 86). On the other hand, **7i** is expected to dissociate extensively to **10** (m/z 86, Scheme 3). Note that these expected products are all observed in the corresponding product spectra (Figure 3).

Triple-Stage (MS^3) Sequential Product Spectra. Structural information on the putative cyclic products **8** is provided by their triple-stage dissociation spectra. Ions **8b** (Figure 4a), **8b-d₃** (Figure 4b), and **8c** (m/z 111, Table 2) dissociate mainly by 30 u neutral loss (most likely CH_2O), whereas consecutive neutral losses of 30 u (CH_2O , m/z 119) and 28 u (CO , m/z 91) dominate for **8d** (Figure 5a). Dissociation initiated by formaldehyde loss is consistent with structures **8** (it should be favorable by the relative position of the two ring-oxygens, as rationalized in Scheme 4), and very contrasting to that of the isomeric ions **11** (Figure 4b and Figure 5b), for which dissociation by C_2H_4O (44 u) loss dominates (Scheme 4).³⁹ Ion **8e** (m/z 99, Table 2) also displays a diverse dissociation chemistry, which includes formaldehyde loss (m/z 69) as a main process, as it is also the case for **8b-d**. Such dissociation again

Scheme 4

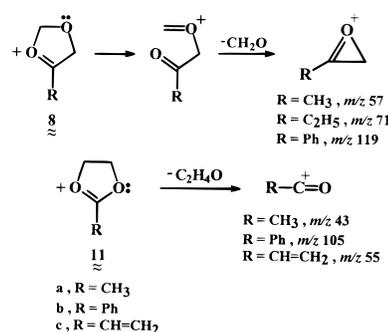


Table 2. Triple-Stage (MS^3) Sequential Product Spectra of the [3 + 2] 1,3-Cycloaddition Products^a

neutral reagent	Q3-mass selected ion (m/z)	dissociation products (m/z) (relative abundance)
2-butanone	87	59(2), 57(100), 45(1), 43(2), 29(3)
	101	73(16), 71(100), 45(3), 43(60)
	155	43(100)
3-pentanone	87	59(2), 57(100), 43(2)
	101	73(12), 71(100), 45(6), 43(42)
fluoroacetone	87	59(2), 57(100), 43(2)
1,1,1-trifluoroacetone	87	59(2), 57(100), 45(1), 43(2), 29(3)
	86	85(45), 58(15), 56(14), 43(100), 28(19)
cyclobutanone	99	71(36), 69(88), 67(63), 45(28), 43(56), 41(100)
	86	85(45), 58(12), 56(11), 43(100), 28(18)

^a Some spectra are shown as figures, see text.

greatly contrasts to the remarkably simple dissociation by C_2H_4O loss (m/z 55) displayed by the isomeric **11c** (spectrum not shown). As expected from the cycloaddition plus dissociation mechanism proposed for formation of **8** and **10** (Schemes 2 and 3), very similar MS^3 spectra are observed for the product ions of m/z 87 (**8b**) obtained from acetone (Figure 4a), 2-butanone, fluoroacetone, and 1,1,1-trifluoroacetone (Table 2); for the m/z 101 ion (**8c**) obtained from both 2-butanone and 3-pentanone; and for **10** (m/z 86) formed in reactions with the two cyclic ketones (Table 2).

Reference Ion. A reference ion (**8d**) was generated from 4-methyl-4-phenyl-1,3-dioxolane,²⁶ and its dissociation chemistry (Figure 5c) compared to that of the putative **8d** of m/z 149 obtained in reactions of **1** with acetophenone (Figure 5a). An almost perfect match between both spectra is observed, which provides strong evidence in favor of structure **8d** and consequently of the operation of the [3 + 2] 1,3-cycloaddition/dissociation mechanism (Scheme 2).

Ab Initio Calculations. Ion–molecule reactions of **1** with the carbonyl compounds investigated appear therefore to take place *via* the two competing pathways presented in Scheme 2. Seeking theoretical support for such reactivity, *ab initio* calculations were performed for the cases of acetone, fluoroacetone, and 1,1,1-trifluoroacetone, and the results are summarized in Table 3 and Figure 6.

Acetone. Both electrophilic addition (**5b**) and cycloaddition (**7b**) of **1** to acetone are shown by the calculations (Figure 6a)

(39) The cyclic structure proposed for the main fragment of ions **8** in Scheme 4 is supported by *ab initio* calculations, which show several $RCOCH_2^+$ ions to undergo spontaneous cyclization during the structure optimization procedure. That acylium ions (RCO^+) are formed from ions **11** upon C_2H_4O loss has been indicated by structurally diagnostic ion–molecule reactions and triple-stage mass spectrometry,^{7a} which show that the cyclic 2-methyl-1,3-dioxolanylium ion forms almost exclusively (99%) the acetyl cation upon collision-induced dissociation.

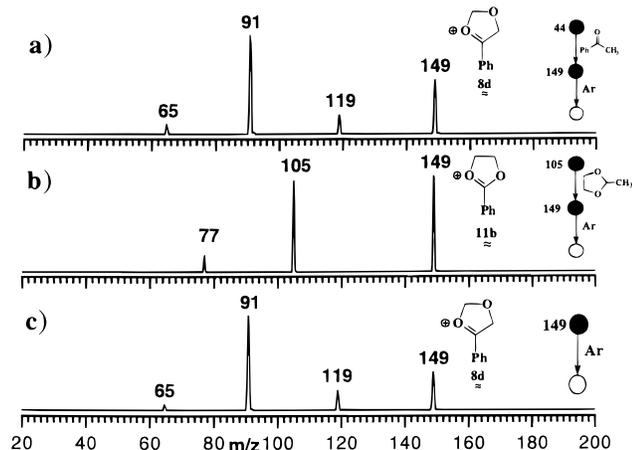


Figure 5. Triple-stage (MS^3) sequential product spectrum of (a) the m/z 149 product (**8d**) formed in ion–molecule reactions of **1** with acetophenone and (b) the isomeric **11b** formed via transacetalization of 2-methyl-1,3-dioxolane with PhCO^+ (m/z 105) and (c) the double-stage dissociation spectrum of the reference ion **8d**. Note the perfect match between the spectra shown in parts a and c and the contrasting dissociation chemistry of isomer **11b** (Figure b).

Table 3. Total and Zero Point Vibrational (ZPE) Energies from *ab Initio* Structure Optimization

species ^a	MP2/6-31G(d,p)//HF/6-31G(d,p) ^b (hartrees)	ZPE ^c (hartree)
1	−152.995 81	0.054 79
5b	−345.601 83	0.150 82
5f^d	−444.603 56	0.145 57
5g	unstable	
6b	−231.403 88	0.115 77
6f	−330.390 54	0.108 81
6g	−528.421 46	0.092 61
7b	−345.589 55	0.156 15
7f^d	−444.597 48	0.150 58
7g	−642.635 75	0.133 95
8b	−305.895 89	0.117 06
CH_3^*	−39.694 61	0.030 85
CH_2F^*	−138.695 94	0.025 00
CF_3^*	−336.742 49	0.013 56
CH_3COCH_3	−192.569 42	0.089 36
$\text{CH}_3\text{COCH}_2\text{F}$	−291.565 82	0.082 48
CH_3COCF_3	−489.616 76	0.066 55
$\text{CH}_2=\text{O}$	−114.181 27	0.028 98

^a Several input geometries were used in the pertinent cases to ensure that the most stable conformation was attained. ^b Spin contaminations of UHF/6-31G(d,p) calculations were acceptable (<0.80) for all the even-electron species. ^c The ZPE values were scaled by 0.89 when calculating the MP2/6-31G(d,p)//HF/6-31G(d,p) + ZPE relative energies used in Figure 6. ^d See Figure 7 for the optimized structure.

to be considerable exothermic processes. Figure 6a also shows that [3 + 2] 1,3-cycloaddition is a less exothermic process, but further dissociation of **7b** by methyl radical loss is a -5.2 kcal/mol exothermic process that leads to the most stable products (**8b** and CH_3^*). Dissociation of the most stable primary product **5b** by $\text{CH}_2=\text{O}$ loss is, on the other hand, 7.1 kcal/mol endothermic from the adduct, hence the overall reaction leading to the CH_2^{*+} transfer product **6b** is a more energy demanding process than cycloaddition. The relative energies and the dissociation thresholds also indicate that once formed, the acyclic adduct **5b** will not undergo cyclization to **7b**, but will preferentially dissociate by formaldehyde loss, which is both a more thermodynamically and entropically favorable process. This result indicates therefore a concerted [3 + 2] 1,3-cycloaddition of **1** to acetone. Note also that both overall reactions are considerably exothermic processes, hence “hot” (high amounts of internal energy) primary cycloadducts should

be formed. This explains the rapid dissociation of the nascent cycloadducts and the observation of only their fragments in the product spectra.

Fluoroacetone. As already stated, it is expected that the strong electron withdrawing fluorine substituent favors cycloaddition both by activating the carbonyl compound toward cycloaddition and by diminishing the nucleophilicity of the carbonyl oxygen. These expectations are clearly confirmed in the *ab initio* potential energy surface diagram for fluoroacetone (Figure 6b). The fluorine substituent leads to a relatively greater stabilization of the primary cycloadduct **7f**, and the difference in energy with respect to the acyclic adduct **5f** drops from 10.7 to 6.6 kcal/mol. In addition, the fluorine substituent decreases considerably the relative stability of the CH_2^{*+} transfer product **6f**, hence this pathway becomes notably more endothermic (15.6 kcal/mol from **5f**). On the other hand, dissociation to **8b** of the cycloadduct **7f** remains exothermic, being -10.2 kcal/mol more thermodynamically favorable than CH_2^{*+} transfer. Therefore, cycloaddition in this case should compete more efficiently with electrophilic addition, as it is indeed observed (Table 1).

1,1,1-Trifluoroacetone. From the results obtained for acetone and fluoroacetone, it is expected that the F_3 -cycloadduct **7g** will be more stable than the acyclic adduct **5g**. In addition, there should be a much greater energy separation of their dissociation thresholds. These expectations are entirely confirmed by the *ab initio* calculations (Figure 6c). In fact, as a likely result of strong deactivation of the ketone toward electrophilic attack, the acyclic adduct **5g** was found by the calculations to be *unstable*, its geometry optimization leading to substantial separation between trifluoroacetone and **1**. Thus, CH_2^{*+} transfer (**6g**) would only be possible by a direct displacement mechanism, which is shown by the calculations to be overall 6.3 kcal/mol endothermic, hence thermodynamically unfavorable. Cycloaddition, on the other hand, remains quite exothermic (-7.5 kcal/mol) as well as further dissociation of the primary cycloadduct **7g** by CF_3^* loss (-3.5 kcal/mol). Consequently, the cycloaddition/dissociation pathway leading to **8b** (m/z 87) and CH_3^* should greatly dominate for 1,1,1-trifluoroacetone, exactly as observed (Figure 2b). The *ab initio* results summarized in Figure 6 are therefore entirely consistent with the interpretation of the reaction as occurring by two competitive and independent reaction channels that are followed by rapid dissociations (Scheme 2).

The *ab initio* optimized structures of the fluoroacetone adducts **5f** and **7f** and their Mulliken charge and odd spin distributions are shown in Figure 7. Note that, as an effect of the electrophilic attack to acetone, charge on the distonic adduct **5f** is mainly concentrated on the binding methylene group, whereas spin density is highly localized at the terminal methylene group. Such distribution is opposed to that of **1**, in which both charge and spin densities are evenly distributed by the two methylene groups.^{30b} Note also the planarity of the boundary methylene group, whereas the binding methylene group is essentially tetrahedral. On the other hand, the cyclic adduct **7f** with conventional ionic structure shows extensive dispersion of the positive charge, whereas spin density is heavily concentrated on the O-3 oxygen atom.

Conclusion

A novel [3 + 2] 1,3-cycloaddition has been observed in gas phase ion–molecule reactions of several carbonyl compounds with the distonic ion $^+\text{CH}_2\text{OCH}_2^-$, that is the ionized form of the simplest, yet unknown carbonyl ylide $^+\text{CH}_2\text{OCH}_2^-$. Cycloaddition competes with electrophilic addition to the carbonyl oxygen and is favored for carbonyl compounds bearing electron

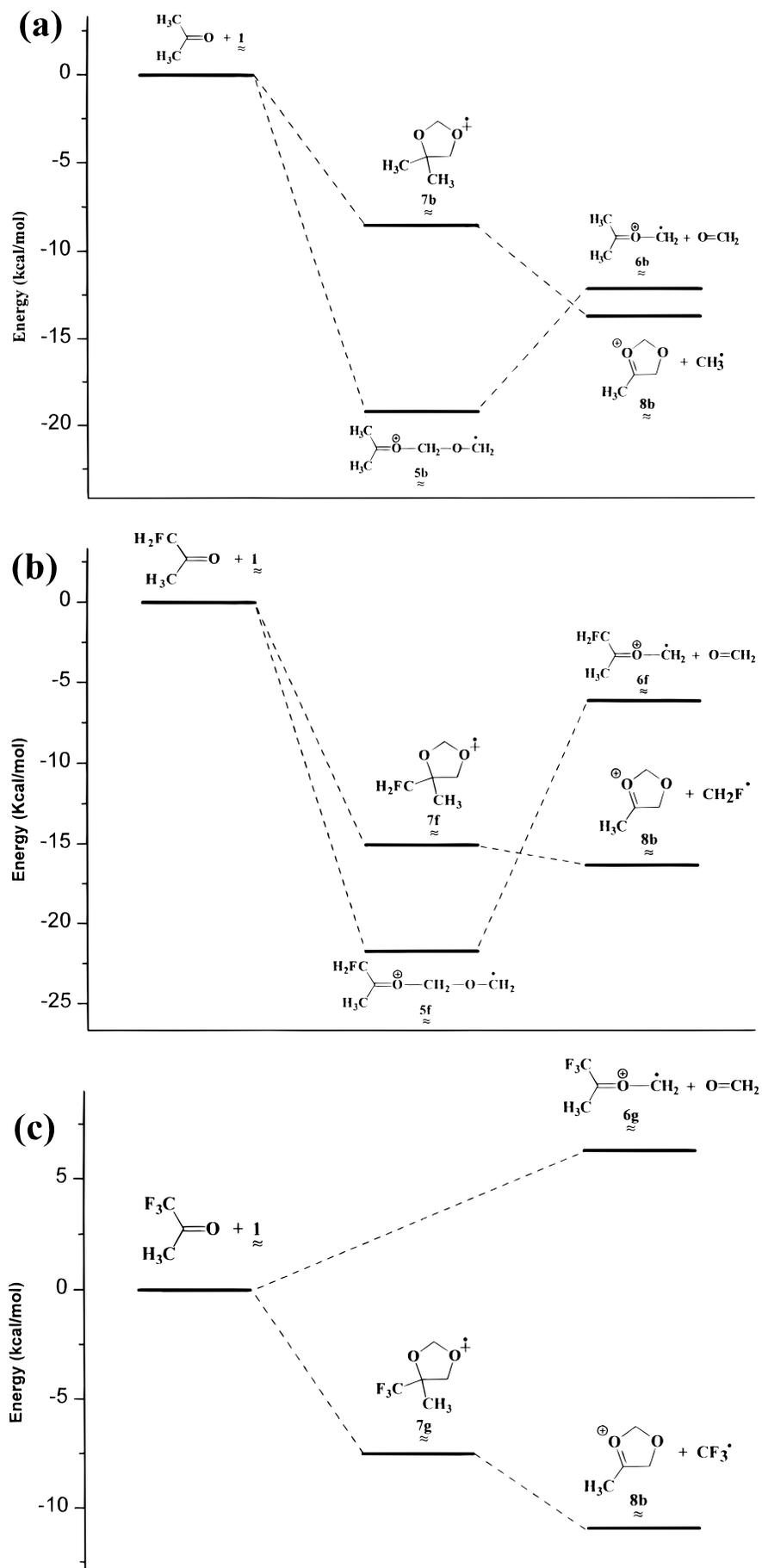


Figure 6. *Ab initio* potential energy surface diagram for the reaction/dissociation sequences of **1** with (a) acetone, (b) fluoroacetone, and (c) 1,1,1-trifluoroacetone calculated at the MP2/6-31G(d,p)/HF/6-31G(d,p) + ZPE level of theory.

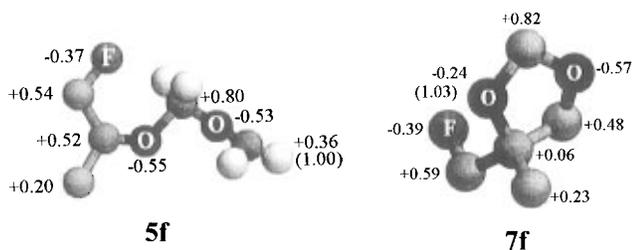


Figure 7. *Ab initio* optimized structures and Mulliken charge and odd spin densities (in parentheses) for the acyclic adduct (**5f**) and the cyclic adduct (**7f**) of fluoroacetone. Most hydrogens are omitted for clarity, whereas the values for the hydrogens were summed unto the heavy atoms.

withdrawing substituents. Both the cyclic and acyclic nascent adducts, due to exothermic reactions, are formed with excess

of internal energy that drive their rapid and complete dissociation to cyclic 4-substituted 1,3-dioxolanium ions and $\text{CH}_2^{+\bullet}$ transfer products, respectively. Characterization of the cycloaddition products has been achieved *via* a systematic study of the reaction performed by multiple stage pentaquadrupole mass spectrometry, whereas the *ab initio* potential energy surface diagrams have provided theoretical support for the operation of the two competing reactions and the favoring of the cycloaddition process by electron-withdrawing substituents.

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