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

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Received May 2, 1995. Revised Manuscript Received April 24, 1996

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 $^{+}$CH$_2$OCH$_2$$^*$ (I) with several carboxyl compounds. The reaction, which competes with electrophilic addition that leads to net CH$_2$$^+$ transfer, occurs across the C=O double bond of acetaldehyde and several acrylic 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 I 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$_5$H$_4$ and C$_2$H$_5$$^*$ yields the ionized 4-methylene-1,3-dioxolanylium and the 4-ethenyl-1,3-dioxolanylium product ions, respectively. A systematic study of this novel reaction and characterization of the product ions carried out via pentaquadrupole (QqQqQ) multiple stage (MS$^2$ and MS$^3$) mass spectrometric experiments provide experimental evidence for the cycloaddition mechanism. The dissociation chemistry observed for the cycloaddition products correlate well with their proposed structures and was compared to that of both isomeric and reference ions. Ab initio MP2/6-31G(d,p)//HF/6-31G(d,p) + ZPE potential energy surface diagrams for the reactions of I with acetone, fluoroacetone, and 1,1,1-trifluoroacetone support the operation of the two competitive reaction pathways, that is CH$_2$$^+$ transfer and [3 + 2] 1,3-cycloaddition/dissociation, and show that the cycloaddiction 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 (M$^+$) 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 acylum ions (RC$^+=O$) with several “s-cis” conjugated dienes.7,8


1,3-Cycloaddition of an Ionized Carbonyl Ylide

They participate as elusive intermediates in thermal and photochemical decomposition of epoxides,10 diazoketones,11a oxadiazolines,11b and ox ae than o nes11c and have been efficiently trapped with several dipolarophiles by 1,3-cycloaddition. 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 $\alpha$-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 stable15 ionized form (I) 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-dioxalan e,15a 1,4-dioxane,15b and ethylene carbonate15c or by ionization followed by rapid C--C ring-opening of ethylene oxide.16

$$\text{O} + \text{O} + \text{R} \rightarrow \text{R} \text{O} \text{O} \text{R}$$

In the present study,17 the gas phase ion--molecule chemistry of $\text{CH}_2\text{OCH}_2^-$ (I) with several carbonyl compounds has been systematically investigated via multiple stage (MS$^2$ and MS$^3$) penta quadrupole (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 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 Extrad [Pittsburgh, PA] penta quadrupole mass spectrometer, which has been described in detail elsewhere.18 The instrument consists basically of three mass analyzing (Q1, Q3, Q5) and two reaction (q2, q4) quadrupoles. Ion I was generated by 70 eV dissociative electron ionization (EI) of 1,3-dioxalan e.15a Ion--molecule reactions of I were performed by MS$^2$ experiments in which I 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 MS$^3$ 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 $2 \times 10^{-6}$ (ion-source), $8 \times 10^{-6}$ (q2), and $6 \times 10^{-5}$ (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 Möller--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),21 and 1,4-dioxaspiro[4,5]decane (11c).21 Ion

(14) Cycloaddition reactions are classified in terms of the number of $\pi$ electrons of each component participating in the reaction. Thus, cycloaddition reactions of 1 ($\text{CH}_2\text{OCH}_2^-$), a $\pi$ electron and a 1,3-coupling species, with 2$\pi$ electron species are termed [3 + 2] 1,3-cycloaddition.
11b was obtained by transacetalization of 2-methyl-1,3-dioxolane with PhCO⁺, which was generated via 70 eV dissociative EI of acetophenone.

Results and Discussion

Structure of the Reactant Ion. Several studies have shown that dissociative EI of 1,3-dioxolane forms 1 as the primary C₂H₄O⁺ fragment and that 1 efficiently transfers ionized methylene (CH₂⁺) to a series of neutral compounds such as nitriles, ketones and pyridines. Theoretical calculations on C₄H₄O⁺ isomers 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 CH₂⁺ 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, being kinetically stable under the present reaction conditions toward both isomerization and dissociation.

Reactions with Carbonyl Compounds. CH₂⁺ Transfer. Reactions of 1 with acetonitrile have been studied earlier, and CH₂⁺ transfer was a main process observed. Under the present experimental conditions, 1 transfers CH₂⁺ to all carbonyl compounds investigated to variable extents (Table 1 and Figures 2–3). Although several alternative structures are possible, structurally specific ion–molecule reactions have shown that the distonic ion (CH₃)₂C=O⁺CH₂⁺ of m/z 72 is formed in CH₂⁺ transfer to acetonitrile (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.


(29) The term “structure” will be used throughout in a restricted sense, to denote connectivity rather than detailed structure.


mainly by net CH$_2$ dissociation products of

trum$_2$ shows a fragment of 70 eV dissociative ionization of 4-methyl-1,3-dioxolane. The mass spec-

chamber (q$_2$), which strongly suggested that

observed when varying significantly the collision pressure inside the reaction

products, that is the CH$_2$ compounds

compounds the ionized 4,4-diaryl-1,3-dioxolane cycloadducts 7. The two observed products, that is the CH$_2$+ 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);$^{24}$ the acetone cycloadduct (7b) a methyl radical (8b, m/z 87);$^{35}$ the 2-butanoxy cycloadduct (7c) both an ethyl (8b, m/z 87) and a 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 radicals$^{37}$ to form 8b of m/z 87. With no exception, ionic products of these observed 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-d$_6$) 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 C$_2$-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 fluoroacetones and consequently disfavor pathway (a) that leads to net CH$_2$+ 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 CH$_2$+ transfer (m/z 72) and moderately by cycloaddition (m/z 87); fluoroacetone (Table 1) reacts by CH$_2$+ 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

<table>
<thead>
<tr>
<th>neutral reactant</th>
<th>protonated$^b$ reagent</th>
<th>CH$_2$+ transfer</th>
<th>CH+ transfer</th>
<th>[3 + 2] 1,3-cycloaddition$^c$</th>
<th>other products</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetaldehyde</td>
<td>45(62)</td>
<td>58(32)</td>
<td>87(100)$^d$</td>
<td>89(18)</td>
<td></td>
</tr>
<tr>
<td>acetone-d$_6$</td>
<td>65(48)</td>
<td>78(100)</td>
<td>90(32)</td>
<td>129(16)$^e$</td>
<td></td>
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<tr>
<td>fluoroacetone</td>
<td>77(36)</td>
<td>90(100)</td>
<td>87(99)</td>
<td>43(21)</td>
<td></td>
</tr>
<tr>
<td>2-butane</td>
<td>73(5)</td>
<td>86(100)</td>
<td>87(94), 101(2)</td>
<td>71(4)</td>
<td></td>
</tr>
<tr>
<td>3-pentane</td>
<td>87(5)</td>
<td>100(52)</td>
<td>101(100)</td>
<td>45(6), 173(13)$^f$</td>
<td></td>
</tr>
<tr>
<td>acetonaphenol</td>
<td>121(8)</td>
<td>134(13)</td>
<td>133(100)</td>
<td>149(55), 119(3), 75(11)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$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.

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: (CH$_3$)$_2$CO+ + H$_2$O → C$_2$H$_4$O-COCH$_3$+ (m/z 87) + CH$_3$. 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-1-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 CF$_3$+ (not CH$_2$+) from 7g is expected when examining, for instance, the mass spectrum of CF$_3$COCH$_3$, and noting the dominance of the CHCO$^+$ fragment.

Dioxaspiro[4,4]nonane ion,27 products expected in these cases. As for the isomeric 1,4-
process, as it is also the case for 8b neutral loss (most likely CH2O), whereas consecutive 
m/z 87 (and its [4,3]-analogue 7i). The bicyclic spiro 1,3-dioxaspiro[4,4]nonane ion 
Triple-stage (MS3) sequential product spectrum of (a) the

Figure 4. Triple-stage (MS3) sequential product spectrum of (a) the m/z 87 (8b) and (b) m/z 90 (8b–d1) products formed in ion–molecule reactions of 1 with acetone and acetone-d6, respectively, and (c) the double-stage dissociation spectrum of the isomeric 11a. Ion 8b eliminates mainly formaldehyde (m/z 57), whereas loss of C2H3O (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 (MS3) Sequential Product Spectra. Structural information on the putative cyclic products 8 is provided by their triple-stage dissociation spectra. Ions 8b (Figure 4a), 8b–d1 (Figure 4b), and 8c (m/z 111, Table 2) dissociate mainly by 30 u neutral loss (most likely CH2O), whereas consecutive neutral losses of 30 u (CH2O, 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 C2H3O (44 u) loss dominates (Scheme 4).29 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 greatly contrasts to the remarkably simple dissociation by C2H3O loss (m/z 55) displayed by the isomeric 11e (spectrum not shown).

Table 2. Triple-Stage (MS3) Sequential Product Spectra of the [3 + 2] 1,3-Cycloaddition Products

<table>
<thead>
<tr>
<th>neutral reagent</th>
<th>Q3-mass selected ion (m/z)</th>
<th>dissociation products (m/z) (relative abundance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butanone</td>
<td>87 59(2), 57(100), 45(1), 43(2), 29(3)</td>
<td></td>
</tr>
<tr>
<td>3-pentanone</td>
<td>101 73(16), 71(100), 45(3), 43(60)</td>
<td></td>
</tr>
<tr>
<td>fluoroacetone</td>
<td>87 59(2), 57(100), 45(2)</td>
<td></td>
</tr>
<tr>
<td>1,1,1-trifluoroacetone</td>
<td>155 43(100)</td>
<td></td>
</tr>
<tr>
<td>cyclobutanone</td>
<td>86 85(45), 58(15), 56(14), 43(100), 28(19)</td>
<td></td>
</tr>
<tr>
<td>cyclopentanone</td>
<td>99 71(36), 69(88), 67(63), 45(28), 43(66), 41(100)</td>
<td></td>
</tr>
<tr>
<td>acetone</td>
<td>86 85(45), 58(12), 56(11), 43(100), 28(18)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Triple-Stage (MS3) Sequential Product Spectra of the [3 + 2] 1,3-Cycloaddition Products

* Some spectra are shown as figures, see text.

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 RCOC2H5+ ions to undergo spontaneous cyclization during the structure optimization procedure. That acylium ions (RCO+) are formed from ions 11 upon C2H3O loss has been indicated by structurally diagnostic ion–molecule reactions and triple-stage mass spectrometry,24 which show that the cyclic 2-methyl-1,3-dioxolanylium ion forms almost exclusively (99%) the acylium cation upon collision-induced dissociation.

![Figure 4](image-url)
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 cycloadition both by activating the carbonyl compound toward cycloaddition and by diminishing the nucleophility 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$_2$$++$ 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 opposite 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 CH$_2$OCH$_2$$++$, that is the ionized form of the simplest, yet unknown carbonyl ylide CH$_2$OCH$_2$. Cycloaddition competes with electrophilic addition to the carbonyl oxygen and is favored for carbonyl compounds bearing electron

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

<table>
<thead>
<tr>
<th>species(^a)</th>
<th>MP2/6-31G(d,p)// HF/6-31G(d,p)(^b) (hartrees)</th>
<th>ZPE(^\prime) (hartrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-152.995 81</td>
<td>0.054 79</td>
</tr>
<tr>
<td>5b</td>
<td>-345.601 83</td>
<td>0.150 82</td>
</tr>
<tr>
<td>5f</td>
<td>-444.603 56</td>
<td>0.145 57</td>
</tr>
<tr>
<td>5g</td>
<td>unstable</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>-231.403 88</td>
<td>0.115 77</td>
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<tr>
<td>6f</td>
<td>-330.390 54</td>
<td>0.101 61</td>
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<td>6g</td>
<td>-528.421 46</td>
<td>0.092 61</td>
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<tr>
<td>7b</td>
<td>-345.589 55</td>
<td>0.156 15</td>
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<td>7f</td>
<td>-444.597 48</td>
<td>0.150 58</td>
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<td>7g</td>
<td>-642.635 75</td>
<td>0.133 95</td>
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<td>8b</td>
<td>-305.895 89</td>
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<td>CH$_2$</td>
<td>-39.694 61</td>
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<td>CH$_3$F</td>
<td>-138.695 94</td>
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<td>CF$_3$</td>
<td>-336.742 49</td>
<td>0.013 56</td>
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<td>CH$_2$COCH$_3$</td>
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<td>CH$_2$COCF$_3$</td>
<td>-489.616 76</td>
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<td>CH$_2$O</td>
<td>-114.181 27</td>
<td>0.028 98</td>
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</tbody>
</table>

\(^{a}\) 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. The ZPE values where scaled by 0.89 when calculating the MP2/6-31G(d,p)// HF/6-31G(d,p) + ZPE relative energies used in Figure 6. \(^{c}\) See Figure 7 for the optimized structure.

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*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 acetonitrile and (b) the isomeric 11b formed via transactealization 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).*
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.
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-dioxolanylium ions and CH₂⁺ 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.

Acknowledgment. This work was supported by the Research Support Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq). This paper is dedicated to Dr. Connie Kascheres for her outstanding contribution to mass spectrometry in Brazil.

JA9514151

**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.