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Double transacetalization of diacylium ions†

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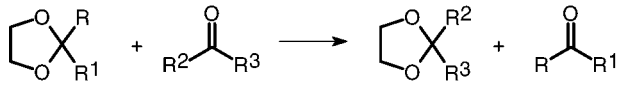
A novel gas-phase reaction of diacylium ions of the O=C=X$^+$=C=O type (X = N, CH) is reported: double transacetalization with cyclic acetals or ketals. The reaction is exothermic and highly efficient, and forms members of a new class of highly charged-delocalized ions: cyclic ionic diketals. Pentaquadrupole double- and triple-stage mass spectrometric (MS^2 and MS^3) experiments reveal the high double transacetalization reactivity of O=C=N$^+$=C=O and O=C=CH$^+$=C=O, whereas the synthesis of differently substituted cyclic ionic diketals is performed in MS^3 experiments via sequential mono- and double transacetalization of O=C=N$^+$=C=O and O=C=CH$^+$=C=O with different acetals. With cyclic acetals, the acylium-thioacylium ion O=C=N$^+$=C=S reacts promptly and selectively by mono-transacetalization at its acylium site, but the free thiacylium site of its cyclic ionic ketal is nearly unreactive by double transacetalization. Therefore, only the acylium site of O=C=N$^+$=C=S can be efficiently protected by transacetalization. Low-energy MS^3 collision-induced dissociation of the cyclic ionic diketals of O=C=N$^+$=C=O and O=C=CH$^+$=C=O sequentially frees each of the protected acylium site to form the mono-derivatized ion, and then the fully deprotected diacylium ion.

KEYWORDS: acylium ions; OCNCO$^+$; OCNCS$^+$; OCCHCO$^+$; ion–molecule reactions; double transacetalization

INTRODUCTION

A cylium ions[1] are known to participate in several condensed-phase reactions as key and highly reactive intermediates, but their detection, trapping and isolation are often not simple tasks. In the gas phase, however, acylium ions (R—C$^+$=O) and their sulfur analogues, the thioacylium ions (R—C$^+$=S), are easily formed, easily isolated and very stable, and a systematic study of the intrinsic gas-phase chemistry of acylium ions has revealed a rich, unique and general reactivity.[2–7] For instance, with conjugated dienes, gaseous acylium ions undergo [4 + 2$^+$] polar cycloaddition;[3] with five- and six-membered cyclic acetals and ketals, transacetalization;[4] with seven-membered cyclic acetals, seven-to-five-membered ring contraction;[5] with diols and analogs, ketalization;[6] and with epoxides, acylium and thioacylium ions promote expansion of the three-membered epoxide ring a five-membered dioxolanylium ring, a reaction known as the 'gas-phase Meerwein reaction.'[7] This structurally characteristic and general reactivity easily distinguishes acylium ions from both isomeric and isobaric species.[2–4]

In solution, carbonyl compounds react promptly with diols and analogs in the presence of an acid catalyst by acetalization (or ketalization) to form cyclic acetals (or ketals). This classical and reversible reaction is widely used to protect carbonyl groups or suitably oriented diol groups in multifunctional molecules. Transacetalization is sometimes advantageously used, and occurs when a second carbonyl compound reacts with an acetal or ketal by replacing the protected carbonyl compound (Scheme 1).



Scheme 1

In the gas phase, transacetalization[4] occurs for many acylium and thioacylium ions in reactions with five- and six-membered cyclic acetals and ketals, and their sulfur and nitrogen analogs, and by pathways that resemble those of condensed-phase transacetalization: the acylium ion 'mimics' the free carbonyl compound, and initial *O*-acylation is followed by a ring-opening–ring-reforming reaction sequence in which the protected neutral carbonyl compound is released and an ionic transacetalization product is formed (Scheme 2).

Gas-phase transacetalization forms ions known as cyclic ionic ketals,[4b] that is, resonance-stabilized five- and six-membered cyclic 1,3-dioxonium ions, and as for the carbonyl compounds in 'neutral' transacetalizations, the acylium ions become protected as cyclic ionic ketals against their most characteristic reactions.[4] When collisionally activated, the cyclic ionic ketals with scrambled oxygens (as demonstrated by ^{18}O labeling)[4b,c] dissociate by releasing the protected acylium ions (Scheme 3), a step that now resembles the reforming acid-catalyzed hydrolysis of neutral acetals and ketals. Hence, just as condensed-phase acid-catalyzed hydrolysis of acetals and ketals frees the protected aldehyde or

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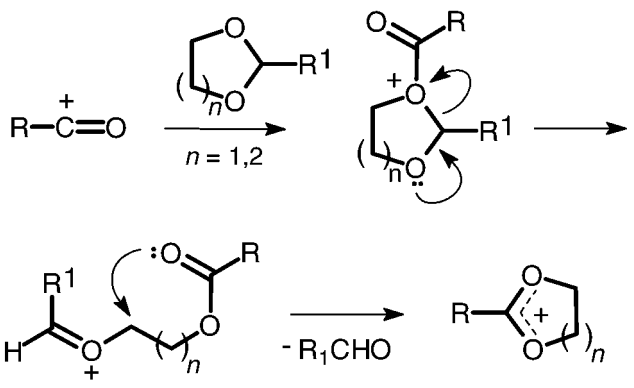


Scheme 2

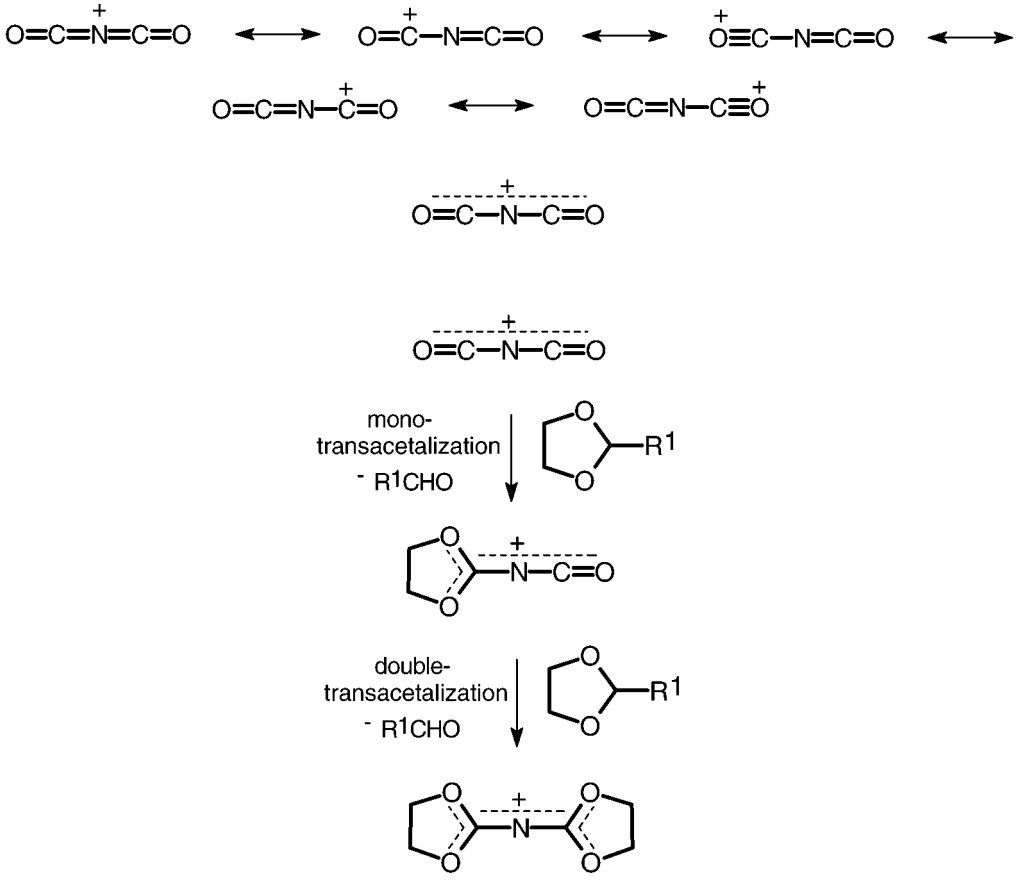
ketone, so gas-phase collision-induced dissociation (CID) of cyclic ionic ketals frees the protected acylium ion.

Scheme 3

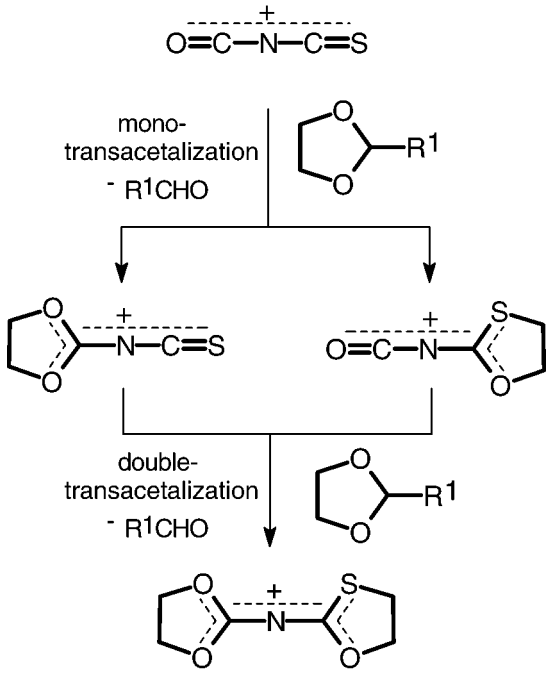
Recently, we showed[4d] that the heterocumulene ion $O{=}C{=}N^+{=}C{=}O$, by far the most stable $C_2NO_2^+$ isomer, displays pronounced acylium ion reactivity with cyclic acetals; it reacts readily by mono-transacetalization. As shown, however, by its resonance forms (see below), $O{=}C{=}N^+{=}C{=}O$[8] is best viewed as a diacylium ion; therefore, the ion should be susceptible not only to mono- but also to double transacetalization (Scheme 4). As predicted by high-level G2(MP2) *ab initio* calculations (see Ref. 4d), $O{=}C{=}N^+{=}C{=}O$ displays two energy minimum structures, rectilinear and angular, and the angular structutre is more stable by 2.6 kcal mol^{-1}. This reaction would then protect both of its acylium sites in the form of a new class of highly charge-delocalized gaseous ions: cyclic ionic diketals (Scheme 4). The *C*-analog diacylium ion $O{=}C{=}CH^+{=}C{=}O$, whose C-3-protonated structure has recently been characterized,[8] should also react similarly, by both mono- and double transacetalization.

The acylium-thioacylium ion $O{=}C{=}N^+{=}C{=}S$, another candidate for double transacetalization, offers a unique case of site selectivity: initial mono-transacetalization could occur at either its acylium or thioacylium site to form two isomeric cyclic ionic ketals (Scheme 5). Then, depending on the reactivity of either the remaining and free acylium or thioacylium site, further transacetalization (double transacetalization) could form, from both cyclic ionic ketal intermediates, the same cyclic ionic diketal of $O{=}C{=}N^+{=}C{=}S$ (Scheme 5).

Mono-transacetalization of $O{=}C{=}N^+{=}C{=}S$ at either its acylium or thioacylium site would form two isomeric cyclic ionic ketals (Scheme 5) indistinguisable by double-stage mass spectrometric (MS^2) analysis. However, it should be possible to verify the site selectivity via triple-stage mass spectrometric (MS^3) experiments since transacetalization of thioacylium ions followed by CID

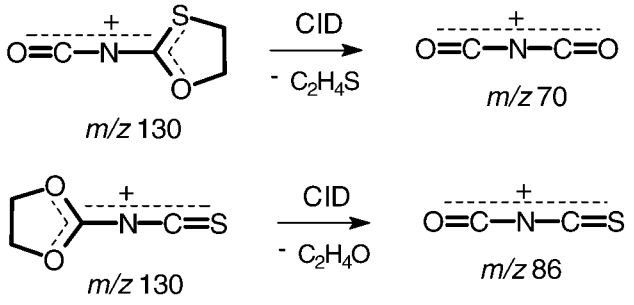


Scheme 4. $O{=}C{=}N^+{=}C{=}O$ resonance forms.



Scheme 5

has been shown to promote complete, or nearly complete, sulfur-by-oxygen replacement.[4c] Mono-transacetalization at the acylium site of O=C=N$^+$=C=S followed by CID of the CS-derivatized isomer should therefore release not the reactant ion O=C=N$^+$=C=S of *m/z* 86 but O=C=N$^+$=C=O of *m/z* 70 (Scheme 6). In sharp contrast, CID of the CO-derivatized isomer would necessarily release O=C=N$^+$=C=S of *m/z* 86 (Scheme 6).



Scheme 6

In this study, MS^2 and MS^3 pentaquadrupole experiments[9] were applied to investigate the reactivity of O=C=N$^+$=C=O, O=C=CH$^+$=C=O and O=C=N$^+$=C=S and the site selectivity of O=C=N$^+$=C=S, towards double transacetalization with cyclic acetals or ketals. *Ab initio* calculations were also employed to access reaction energetics and to rationalize reactivity trends and site selectivities. Both O=C=N$^+$=C=O and O=C=CH$^+$=C=O are found to react to great extents by double transacetalization to form two members of a new class of highly charge-delocalized gaseous ions, cyclic ionic diketals.

EXPERIMENTAL

The gaseous ions were produced, reacted, and their products analyzed via MS^2 and MS^3 experiments performed with an Extrel (Pittsburgh, PA, USA) pentaquadrupole mass spectrometer.[10] The instrument, denoted $Q_1q_2Q_3q_4Q_5$, is composed of a sequential arrangement of three mass-analyzing (Q1, Q3, Q5) and two 'r.f.-only' ion-focusing reaction quadrupoles (q2, q4). By 70 eV electron ionization (EI), appropriate precursors form the reactant acylium ions: ethoxycarbonyl isocyanate forms O=C=N$^+$=C=O,[11] benzoylacetone[8] forms O=C=CH$^+$=C=O and ethoxycarbonyl thyoisocyanate[12] forms O=C=N$^+$=C=S. When performing MS^2 ion–molecule reactions, Q1 was used to mass select the ion of interest for further reactions in q2 with a selected neutral reagent. Ion translational laboratory energies were set to near 1 eV as calibrated by the *m/z* 39 : 41 ratio in neutral ethylene–ionized ethylene reactions.[13] Product ion mass spectra were acquired by scanning Q5, while operating Q3 in the broadband r.f.-only mode. The target gas pressures in q2 caused typical beam attenuations of 50–70%, i.e. multiple collision conditions were used, which increase reaction yields and promote collisional quenching of both the reactant and product ions.[9]

For the MS^3 experiments,[9,14] Q3 is used to mass select a q2 product ion of interest for further 15 eV collision dissociation with argon in q4, while scanning Q5 for mass spectra acquisition. The 15 eV collision energies were taken as the voltage difference between the ion source and the collision quadrupoles. The indicated pressures in each differentially pumped region were typically 2×10^{-6} (ion source), 8×10^{-6} (q2) and 8×10^{-5} Torr (q4), respectively (1 Torr = 133.3 Pa).

Energies and optimized geometries were obtained by molecular orbital calculations using Gaussian 94.[15] First, the geometries were fully optimized at the HF/6–311G(d,p) level of theory,[16] then improved energies were obtained by using single-point calculations at the 6–311G(d,p) level, whereas incorporating valence electron correlation calculated by second-order Møller–Plesset (MP2) perturbation theory.[17] This procedure is denoted MP2/6–311G(d,p)//HF/6–311G(d,p).

RESULTS AND DISCUSSION

O=C=N$^+$=C=O

Mono- and double transacetalization via MS^2 experiments. Figure 1 compares the MS^2 product ion mass spectrum for reactions of O=C=N$^+$=C=O with the cyclic acetal 2-methyl-1,3-dioxolane performed at two different, and low, collision energies. When using ~1 eV collisions,[13] and relatively high pressure of the neutral reactant in q2, both the mono- (*m/z* 114) and double transacetalization products (*m/z* 158) of O=C=N$^+$=C=O are readily formed. When using the same 1 eV energy but lower q2 pressures, the mono-transacetalization product of *m/z* 114 is formed almost exclusively; using even higher q2 pressures, *m/z* 114 is converted nearly completely to

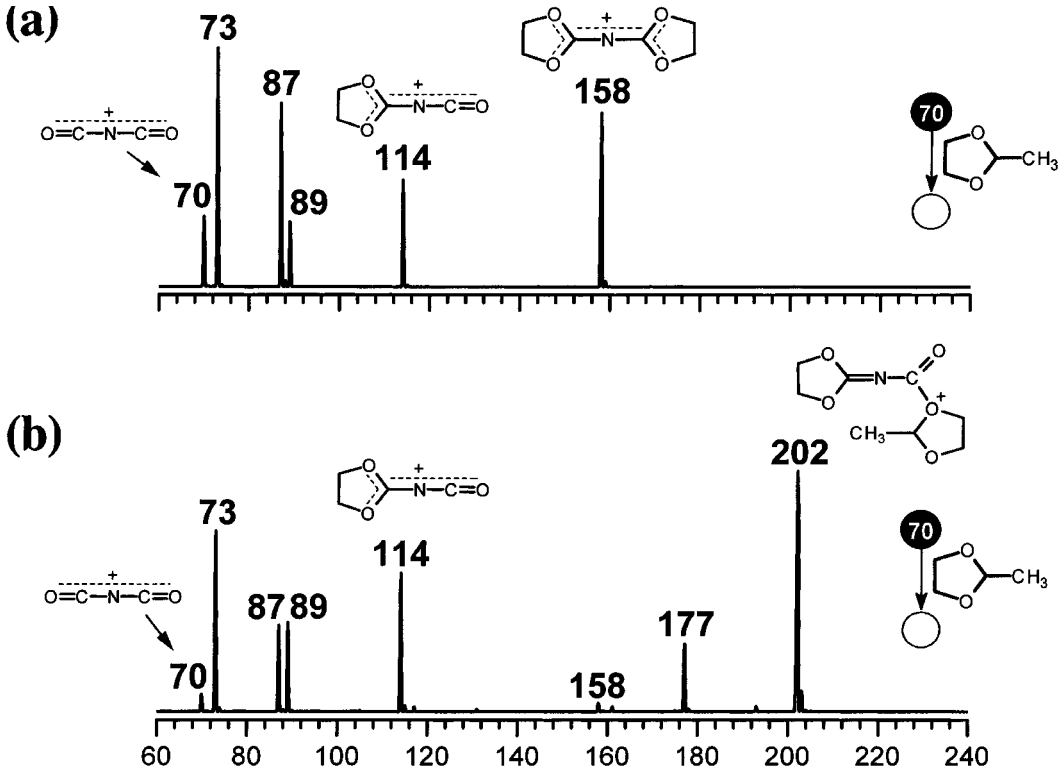
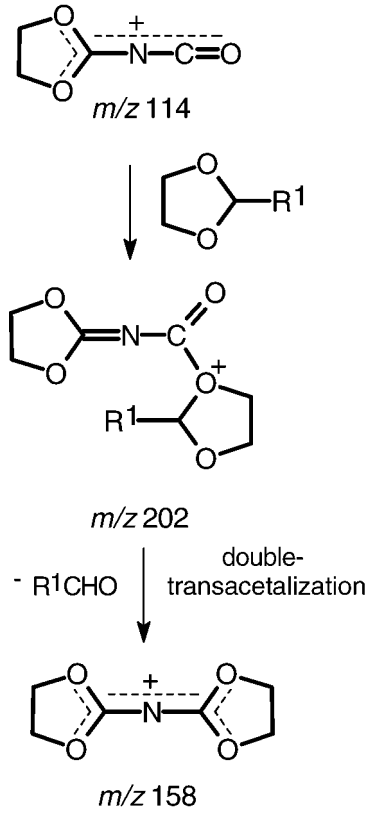


Figure 1. Double-stage (MS^2) product ion mass spectra for reactions of $O{=}C{=}N^+{=}C{=}O$ with 2-methyl-1,3-dioxolane under relatively high pressures in q2 and at (a) ~1 eV and (b) ~0 eV laboratory collision energies. In (b), *m/z* 177 is the proton-bound dimer of 2-methyl-1,3-dioxolane, a weakly bonded species also favored at ~0 eV collision energies.

m/z 158. This product control indicates that the mono-transacetalization product of $O{=}C{=}N^+{=}C{=}O$ reacts promptly by double transacetalization, but the reactivity of its free acylium site decreases considerably after mono-transacetalization. The other ions are the formal hydride (*m/z* 87) and methanide (*m/z* 73) abstraction products, and protonated 2-methyl-1,3-dioxolane of *m/z* 89. The latter is formed, owing to multiple collisions, most likely by secondary reactions of 2-methyl-1,3-dioxolane with the primary product ions.

For $O{=}C{=}N^+{=}C{=}O$ therefore, double transacetalization depends strongly on the collision energy, and occurs only when this energy is set within a very narrow range centered near 1 eV. If the collision energy is slightly increased to ~3 eV or higher, no reaction occurs; if slightly decreased to ~0 eV [Fig. 1(b)], mono-transacetalization still occurs readily (*m/z* 114) but double transacetalization is interrupted at the step that forms the second adduct with 2-methyl-1,3-dioxolane of *m/z* 202 (Scheme 7). Probably under these so low, near-zero eV energy collision conditions, the second adduct is either quenched or not sufficiently collisionally activated, hence, it fails to retain (or to acquire) enough internal energy to dissociate by the loss of acetaldehyde, and very little of the double transacetalization product of *m/z* 158 is formed [Fig. 1(b)].

Double transacetalization via MS^3 experiments. Double transacetalization of $O{=}C{=}N^+{=}C{=}O$ was also accomplished via an MS^3 experiment (Fig. 2). The ion of *m/z* 70 was mass selected by Q1 and reacted in q2 with 2-methyl-1,3-dioxolane with 1 eV collisions, and at a q2 pressure that maximizes mono-transacetalization. The product ion of *m/z* 114 was then mass selected by Q3 and further reacted with ~1 eV collisions with 2-methyl-1,3-dioxolane in q4, while scanning Q5. As the resulting mass spectrum shows (Fig. 2), the cyclic ionic ketal



Scheme 7

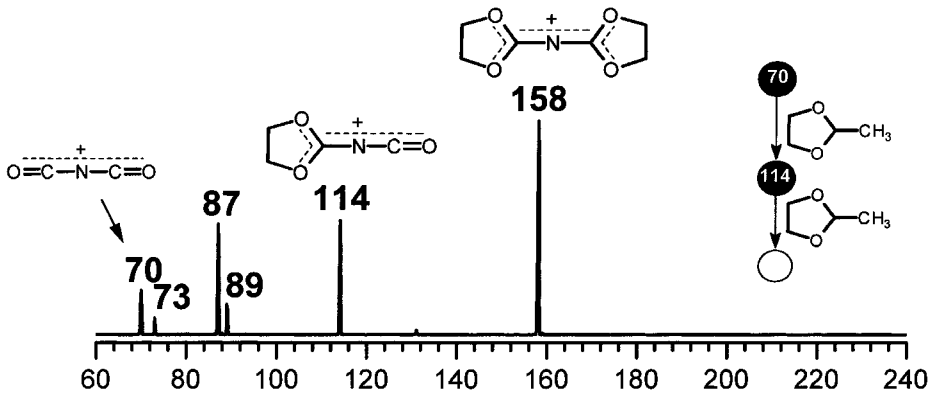
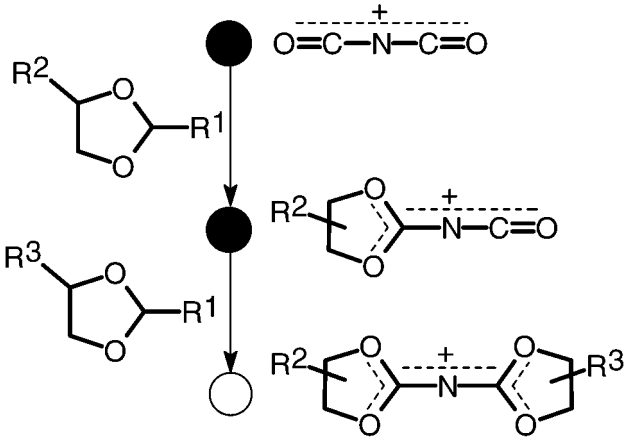


Figure 2. Triple-stage (MS^3) sequential product ion mass spectrum for reactions of $O{=}C{=}N^+{=}C{=}O$ (*m/z* 70) with 2-methyl 1,3-dioxolane in q2, and of its mono-transacetalization product (*m/z* 114) in q4.

of *m/z* 114 resulting from mono-transacetalization of $O{=}C{=}N^+{=}C{=}O$ reacts readily by double transacetalization at its free (less but still considerably reactive) acylium site to form the cyclic ionic diketal of *m/z* 158. To limited extents, the product ion of *m/z* 114 also dissociates to $O{=}C{=}N^+{=}C{=}O$ of *m/z* 70, and forms the formal hydride (*m/z* 87) and methanide (*m/z* 73) abstraction products ions, whereas secondary reactions form protonated 2-methyl-1,3-dioxolane of *m/z* 89.

MS^3 synthesis of differently substituted cyclic ionic diketals. The MS^3 experiment of Fig. 2 indicates that controlled double transacetalization with two differently substituted cyclic acetals (or ketals) could be used to form differently substituted cyclic ionic diketals (Scheme 6). This unique MS^3 synthesis was therefore demonstrated for $O{=}C{=}N^+{=}C{=}O$ by reactions with 2-methyl-1,3-dioxolane in q2 and with 4-methyl-1,3-dioxolane in q4 (Scheme 8, $R^2{=}CH_3$, $R^3{=}H$), and also with 4-methyl-1,3-dioxolane in q2 and with 2-methyl-1,3-dioxolane in q4 (Scheme 8, $R^2{=}H$, $R^3{=}CH_3$). The same double transacetalization product, differently substituted cyclic ionic diketal of *m/z* 172 was readily formed in both experiments (mass spectra not shown).

Double transacetalization with a cyclic ketal. 2-Ethyl-2-methyl-1,3-dioxolane is a cyclic ketal that according to the mechanism depicted in Scheme 2 should react with $O{=}C{=}N^+{=}C{=}O$ to form the same mono and double transacetalization products as those formed with the cyclic acetal



Scheme 8

2-methyl-1,3-dioxolane. Indeed, under ~1 eV collisions, the two expected product ions of *m/z* 114 and 158 were formed to great extents (Fig. 3) together with the formal hydride (*m/z* 115), methanide (*m/z* 101) and ethanide (*m/z* 87) abstraction products and protonated 2-ethyl-2-methyl-1,3-dioxolane of *m/z* 117.

$O{=}C{=}CH^+{=}C{=}O$

The diacylium ion $O{=}C{=}CH^+{=}C{=}O$, C-3-protonated carbon suboxide,[8] is found to display a reactivity similar

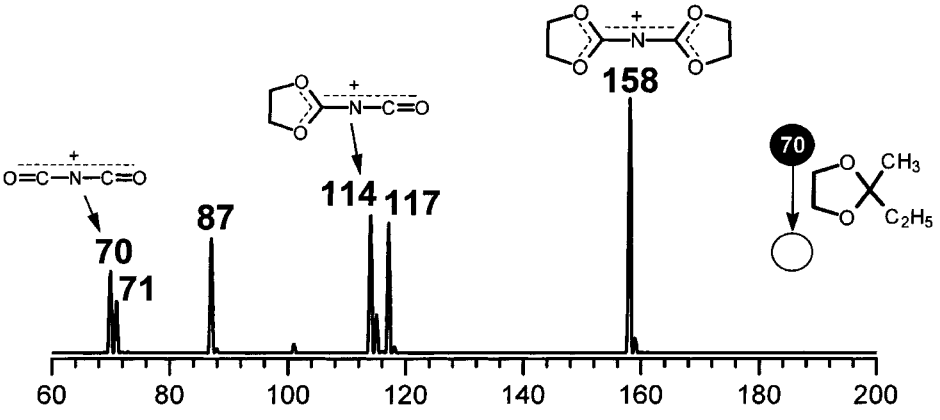


Figure 3. Double-stage (MS^2) product ion mass spectrum for reactions of $O{=}C{=}N^+{=}C{=}O$ with 2-ethyl-2-methyl-1,3-dioxolane at ~1 eV laboratory collision energy.

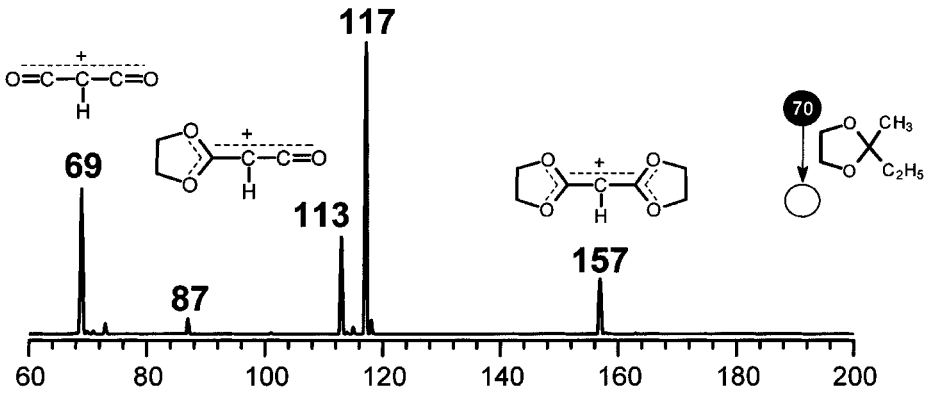


Figure 4. Double-stage (MS^2) product ion mass spectrum for reactions of $O{=}C{=}CH^+{=}C{=}O$ with 2-ethyl-2-methyl-1,3-dioxolane under ~1 eV laboratory collision energy.

to that of $O{=}C{=}N^+{=}C{=}O$. In MS^2 reactions with 2-ethyl-2-methyl-1,3-dioxolane (Fig. 4), the mass-selected $O{=}C{=}CH^+{=}C{=}O$ forms both the mono- (*m/z* 113) and the double transacetalization products (*m/z* 157) to considerable extents. However, as expected for a potential proton-donor ion, $O{=}C{=}CH^+{=}C{=}O$ also readily protonates the neutral ketal to form the produc ion of *m/z* 117.

That $O{=}C{=}CH^+{=}C{=}O$ undergoes double transacetalization, at its two acylium sites, is therefore additional evidence for a C-3-protonated, diacylium ion structure:[8] the C-2-protonated carbon suboxide isomer $O{=}C{=}C^+{-}CH{=}O$ is not an acylium ion and the *O*-protonated isomer $O{=}C^+{-}C{\equiv}C{-}OH$[8] is a mono-acylium ion that should be therefore limited to mono-transacetalization.

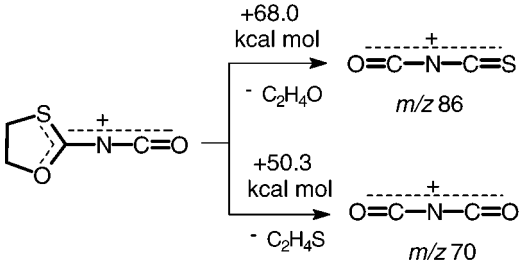
$O{=}C{=}N^+{=}C{=}S$

The cumulenic ion $O{=}C{=}N^+{=}C{=}S$ has recently been formed and characterized in the gas phase.[12a] With 2-methyl-1,3-dioxolane, this interesting acylium-thioacylium ion reacts uniquely (Fig. 5): it readily forms the mono-transacetalization product (*m/z* 130) but little of the double transacetalization product (*m/z* 174), even when high pressures of the neutral reactant are used. These findings (and the MS^3 data discussed below) therefore suggest a contrasting reactivity for $O{=}C{=}N^+{=}C{=}S$: its acylium site is very reactive towards transacetalization but its thioacylium site is nearly unreactive.

That $O{=}C{=}N^+{=}C{=}S$ displays limited double transacetalization reactivity was also demonstrated by an MS^3 experiment; when its q2 mono-transacetalization product of *m/z* 130 was mass selected by Q3 and reacted with 2-methyl-1,3-dioxolane in q4, the cyclic ionic diketal of *m/z* 174 was formed, but to a very limited extent (mass spectrum not shown).

MS^3 CID experiments

When mass selected by Q3 and further dissociated by 15 eV collisions with argon in q4, the cyclic ionic ketals formed by mono-transacetalization of $O{=}C{=}N^+{=}C{=}O$, $O{=}C{=}CH^+{=}C{=}O$ and $O{=}C{=}N^+{=}C{=}S$ [Fig. 6(a)] dissociate extensively and exclusively by releasing the respective precursor ions. For $O{=}C{=}N^+{=}C{=}S$, therefore, since no sulfur-by-oxygen replacement is observed [Fig. 6(a)] and CID frees exclusively the reactant ion (Scheme 4), mono-transacetalization must occur selectively at its acylium site (Scheme 3). Note: assuming that ethylene oxide and ethylene sulfide are the respective neutral products, MP2/6–311G(d,p)//HF/6–311G(d,p) *ab initio* calculations predict, for the cyclic ionic ketal of $O{=}C{=}N^+{=}C{=}S$ formed by mono-transacetalization at the thioacylium site, a dissociation threshold to $O{=}C{=}N^+{=}C{=}O$ 17.7 kcal mol^{-1} less endothermic, and therefore more favorable, than that to $O{=}C{=}N^+{=}C{=}S$ (see below).



The ionic products formed by double transacetalization of $O{=}C{=}N^+{=}C{=}O$ [Fig. 6(b)] and $O{=}C{=}CH^+{=}C{=}O$ [Fig. 6(c)], that is, the first members of the new class of cyclic ionic diketals, dissociate as expected: CID frees sequentially each of the protected acylium sites to form respectively the mono-derivatized ions of *m/z* 114 and 133, and then the fully deprotected diacylium ions of *m/z* 70 and 69.

Ab initio calculations

Reaction energetics: O=C=N⁺=C=O. Figure 7 displays an MP2/6–311G(d,p)//HF/6–311G(d,p) *ab initio* potential energy diagram for mono- and double transacetalization of $O{=}C{=}N^+{=}C{=}O$ with 2-methyl-1,3-dioxolane. The calculations predict initial *O*-acylation to be exothermic by -39.5 kcal mol^{-1} (1 kcal = 4.184 kJ); in fact, the *O*-acylated product was found to be unstable and to undergo spontaneous ring opening to form the corresponding acyclic oxonium ion intermediate (Scheme 1). Further acetaldehyde loss and re-cyclization are, from the adduct, endothermic by $+6.4$ kcal mol^{-1}, but overall (from the reactants) exothermic by -33.3 kcal mol^{-1}, and hence

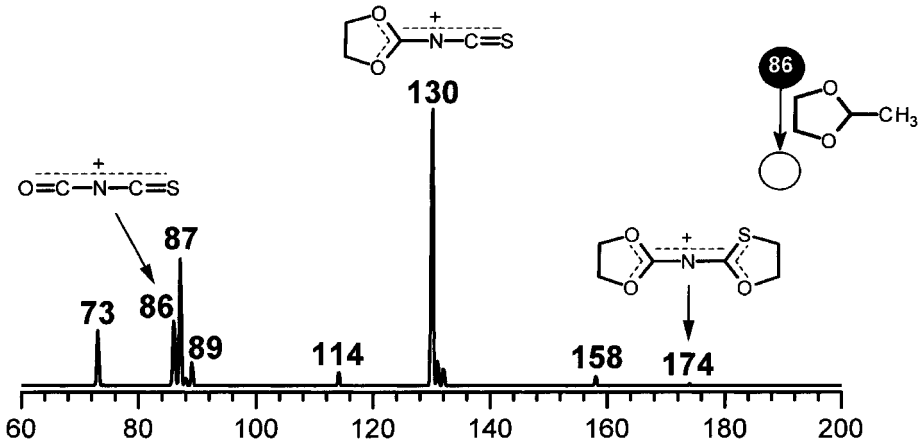


Figure 5. Double-stage (MS^2) product ion mass spectrum for reactions of O=C=N$^+$=C=S with 2-methyl-1,3-dioxolane under ~1 eV laboratory collision energy.

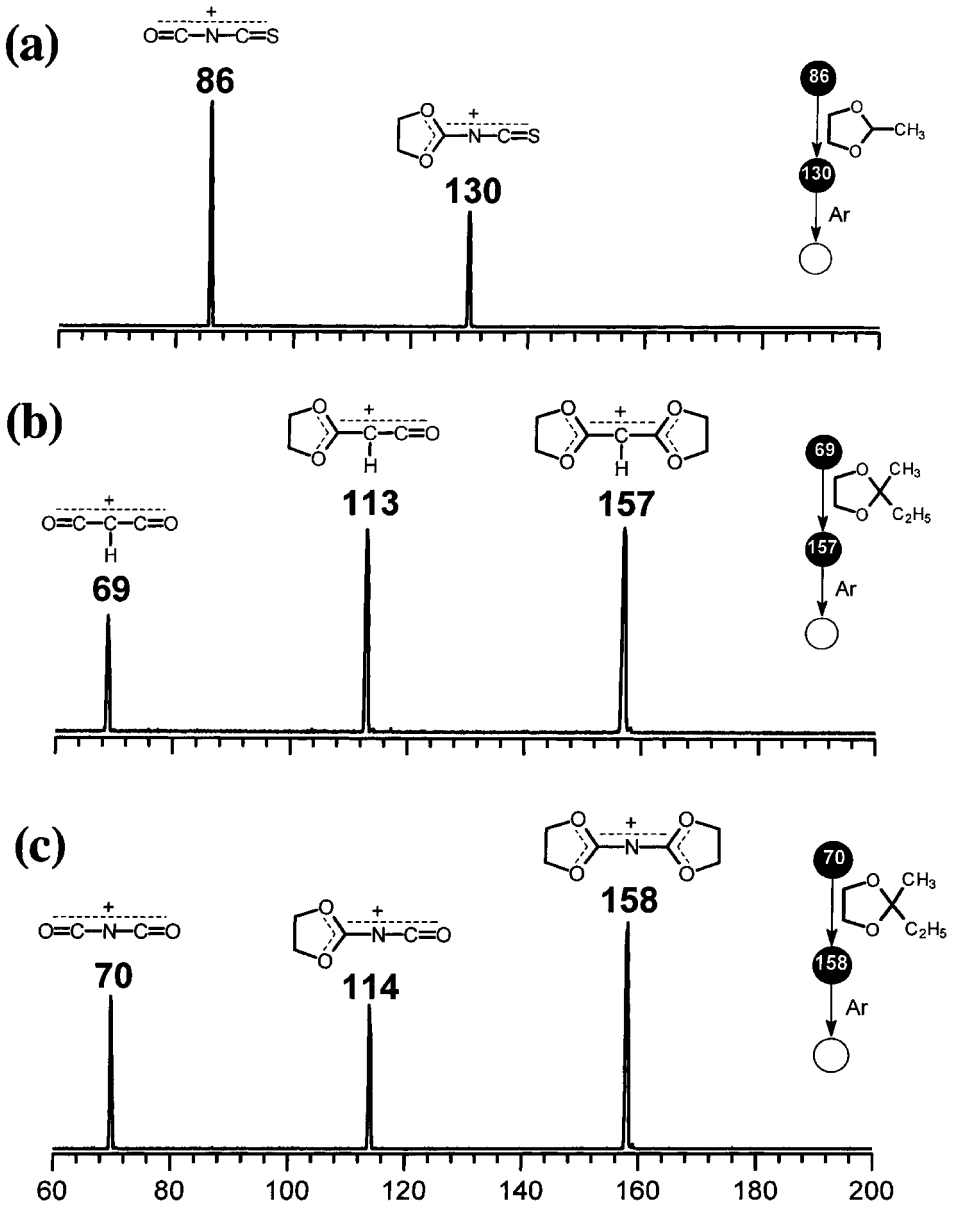


Figure 6. Triple-stage (MS^3) sequential CID product ion mass spectra of (a) the mono-transacetalization product of O=C=N$^+$=C=S and the double transacetalization products of (b) O=C=N$^+$=C=O and (c) O=C=CH$^+$=C=O.

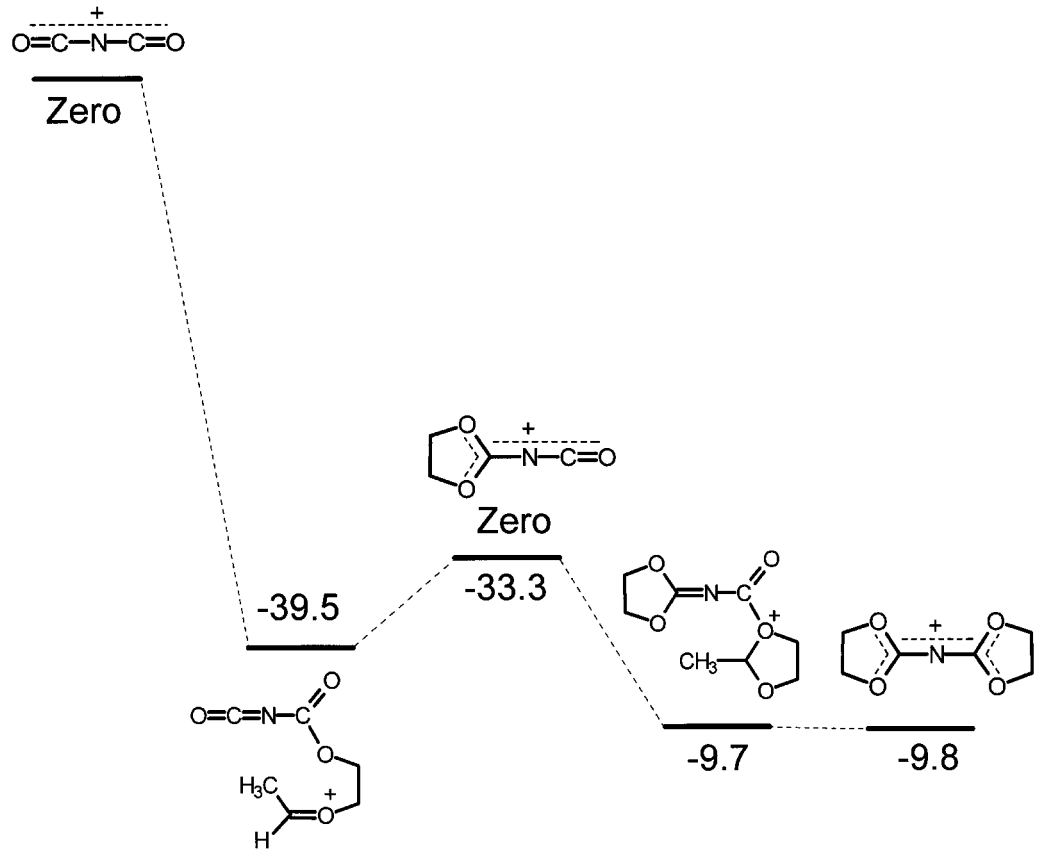


Figure 7. MP2/6–311G(d,p)//HF/6–311G(d,p) *ab initio* potential energy diagram for both mono- and double transacetalization of O=C=N$^+$=C=O. Energies are given in kcal mol^{-1}. Note that two independent reactions are being considered, hence the *mono*-transacetalization product is the zero energy reference for double transacetalization. Neutral reactants and products are omitted, for clarity. Reaction barriers were not estimated, and are not indicated. The first *O*-acylated adducts was shown by the calculations to undergo spontaneous ring opening. The electronic energies of the species, in hartrees, are as follows: O=C=N$^+$=C=O (−280.45874), 2-methyl-1,3-dioxolane (−306.89147), first *O*-acylated adduct (−587.41315), acetaldehyde (−153.44077), mono-transacetalization product (−433.96246), second *O*-acylated adduct (−740.87266), double transacetalization product (−587.43191).

thermodynamically favorable. The second, double transacetalization follows a similar (but less exothermic) pattern; the stable *O*-acylated product (−9.7 kcal mol^{-1}) and the final double transacetalization product (−9.8 kcal mol^{-1}) are formed in exothermic, thermodynamically favored processes.

These energy trends therefore agree with the experimental results: the second *O*-acylation is much less exothermic than the first *O*-acylation, and this reduced exothermicity agrees with the decreased (but still pronounced) double transacetalization reactivity of the free acylium site of diacylium ions after mono-transacetalization. Likewise, as the second *O*-acylation is just slightly exothermic, the resulting stable adduct is formed with less internal energy and is therefore more likely to be either quenched or not sufficiently activated by low-energy collisions; then, if too low, near-zero collision energies are used [Fig. 1(b)], double transacetalization is not completed, and is interrupted at the second *O*-acylation step.

O=C=N$^+$=C=S. Figure 8 displays an MP2/6–311G(d,p)//HF/6–311G(d,p) *ab initio* potential energy diagram for mono- and double transacetalization of O=C=N$^+$=C=S with 2-methyl-1,3-dioxolane. The calculations predict that O=C=N$^+$=C=S very preferentially and hence selectively acylates the neutral acetal via its acylium site: acylation via the thioacylium site is exothermic by −16.1 kcal mol^{-1} and via the acylium site by −35.0 kcal mol^{-1}. The energy trend reverses, however, for the next reaction step of acetaldehyde loss/recyclization: mono-transacetalization at the acylium site of O=C=N$^+$=C=S is overall exothermic by −25.2 kcal mol^{-1} and at the thioacylium site by −33.6 kcal mol^{-1}. Since mono-transacetalization occurs exclusively at its acylium site [Fig. 6(a) and Scheme 2], most likely the rate-limiting step for mono-transacetalization of O=C=N$^+$=C=S with cyclic acetals is the initial *O*-acylation.

Figure 8 also shows that, in accord with the limited double transacetalization reactivity of the cyclic ionic ketal of O=C=N$^+$=C=S, *O*-acylation (the rate-limiting step) by the remaining, free thiacylium site is endothermic by +0.6 kcal mol^{-1}, and therefore thermodynamically unfavorable.

Structures of O=C=N$^+$=C=O and its cyclic ionic ketal and ionic diketal forms. Figure 9 compares *ab initio* MP2/6–311G(d,p)//HF/6–311G(d,p) charge distributions, major bond lengths and angles for O=C=N$^+$=C=O and its mono- and double transacetalization products. The most stable form of O=C=N$^+$=C=O is bent[8] (137.1°), and characterized by short cumulenic double bonds (NC of 1.24 Å and CO of 1.10 Å). The diacylium ion nature of O=C=N$^+$=C=O is also evident: both CO bonds (1.10 Å) are as those of mono-acylium ions,[4] and the CO groups concentrate most of the positive charge (+0.74).

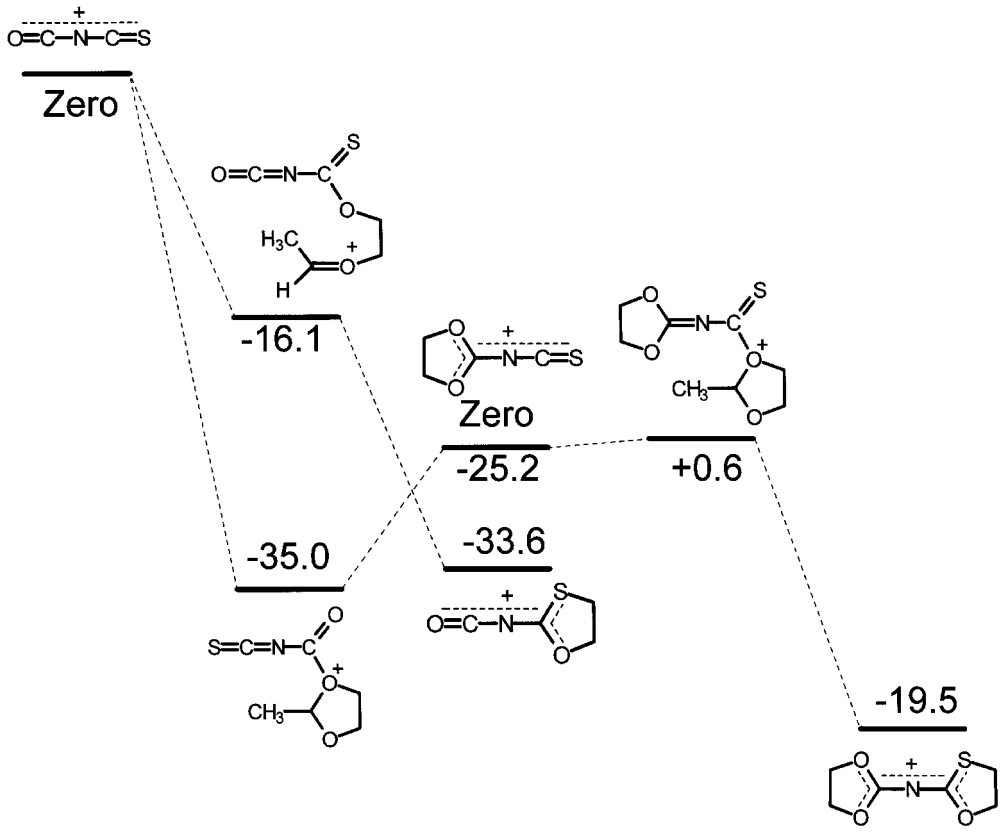


Figure 8. MP2/6–311G(d,p)//HF/6–311G(d,p) potential energy diagram for both mono- and double transacetalization of O=C=N$^+$=C=S. Energies are given in kcal mol^{-1}. Note that two independent reactions are being considered, hence the most favorable mono-transacetalization product is the zero-energy reference for double transacetalization. Neutral reactants and products are omitted, for clarity. Reaction barriers were not estimated, and are not indicated. The electronic energies of the species, in hartrees, are as follows: O=C=N$^+$=C=S (−603.05280), 2-methyl-1,3-dioxolane (−306.89147), first OCO-acylated adduct (−909.98454), first SCO-acylated adduct (−909.97000), acetaldehyde (−153.44077), mono-CO-transacetalization product (−756.54366), mono-CS-transacetalization product (−756.55721), second SCO-acylated adduct (−1063.43415), double transacetalizatiion product (−910.02536).

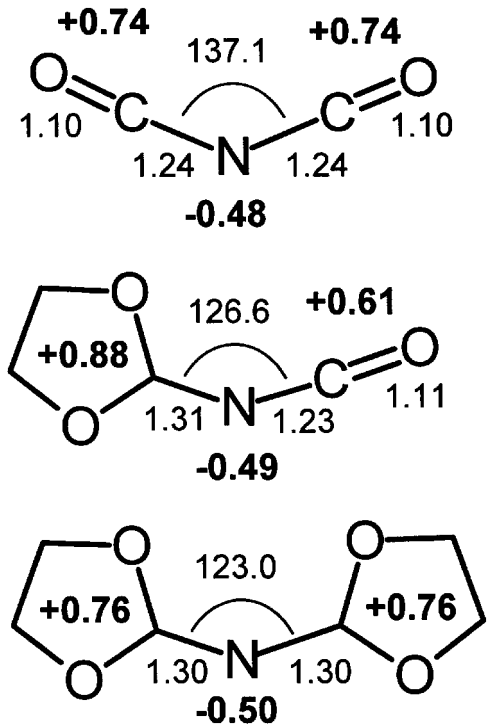


Figure 9. MP2/6–311G(d,p)//HF/6–311G(d,p) major bond lengths (in Å) and angles (in degrees), and Mülliken charges on nitrogen and on the two N-connected subunits of O=C=N$^+$=C=O, and of its mono- and double transacetalization products.

In the cyclic ionic ketal of O=C=N$^+$=C=O, as the result of mono-ketalization of a CO group, the O_2C—N bond is considerably elongated to 1.31 Å whereas the positive charge, owing to more effective delocalization, is more concentrated in the 1,3-dioxolane ring (+0.88). However, the mono-transacetalization product stills displays a pronounced mono-acylium ion nature: the CO bond of its free carbonyl group is still as short as those in O=C=N$^+$=C=O and this group still bears a significant portion of the positive charge (+0.61).

In the cyclic ionic diketal of O=C=N$^+$=C=O, as the cumulenic nature of the precursor diacylium ion is now totally lost, both symmetric NC bonds are elongated to 1.30 Å, the CNC angle is enlarged to 123.0° and, as expected, the positive charge is evenly distributed by, and mainly concentrated in, the two ketal rings.

CONCLUSION

A novel, overall exothermic and efficient gas-phase reaction has been demonstrated for diacylium ions: double transacetalization with cyclic acetals. This unique reaction, which adds to the rich gas-phase chemistry of acylium ions, opens up access to a new class of

gaseous, highly charge-delocalized ions: cyclic ionic diketals. For the diacylium ions $O{=}C{=}N^{+}{=}C{=}O$ and $O{=}C{=}CH^{+}{=}C{=}O$, the reactivity of the free acylium site towards double transacetalization is still pronounced, but decreases considerably after mono-transacetalization. Therefore, it is possible to control the reaction to form either the mono- or the double transacetalization products, or both, or to form sequentially and efficiently via MS^3 experiments differently substituted cyclic ionic diketals via controlled mono-transacetalization with a cyclic acetal, and then double transacetalization with a second acetal.

As indicated by the reactivity of $O{=}C{=}N^{+}{=}C{=}S$, the thioacylium site of acylium-thioacylium ions is unreactive or nearly unreactive towards both mono- and double transacetalization. Its acylium site react readily, however, by mono-transacetalization.

In a process that resembles the reforming acid-catalyzed condensed-phase hydrolysis of neutral acetals and ketals in solution, gas-phase low-energy CID of the cyclic ionic diketals sequentially frees each of the derivatized, protected acylium site of the diacylium ions; it re-forms the mono-derivatized ion, and then the fully deprotected ion.

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