ELSEVIER International Journal of Mass Spectrometry 212 (2001) 445–454 www.elsevier.com/locate/ijms

Cyclization of acylium ions with nitriles: gas-phase synthesis and characterization of 1,3,5-oxadiazinium ions

Eduardo C. Meurer, Luiz Alberto B. Moraes, Marcos N. Eberlin*

State University of Campinas–UNICAMP, Institute of Chemistry CP6154, 13083-970 Campinas, SP Brazil

Received 14 February 2001; accepted 15 March 2001

Abstract

Gas phase reactions of mass-selected acylium ions [CH_3–C^+=O (**1**), CH_2=CH–C^+=O (**2**), C_6H_5–C^+=O (**3**), and $(CH_3)_2N$–C^+=O (**4**)] with nitriles (CH_3CN, C_2H_5CN, CH_2=CHCN, and C_6H_5CN) were investigated using pentaquadrupole multiple-stage mass spectrometry. In analogy with the solution behavior, the ions were found to react readily with benzonitrile by cyclization via double nitrile addition to form aromatic 1,3,5-oxadiazinium ions. Cyclization with acetonitrile, propionitrile, and acrylonitrile is less general and occurs readily only for **4**, by far the most reactive acylium ion tested. In "one-pot" reactions of **4** with two-component nitrile mixtures, cyclization via double nitrile addition occurs readily and forms both equally and differently 4,6-disubstituted isomeric 1,3,5-oxadiazinium ions. Using MS^3 experiments, the 1,3,5-oxadiazinium ions were mass-selected and then either reacted with nitrogen nucleophiles or dissociated by low-energy collisions with argon. The nucleophiles add readily to the ions, whereas the symmetry of the 1,3,5-oxadiazinium ring allows two competitive dissociation pathways: double retro-addition that re-forms the reactant acylium ion, or an analogous dissociation that, formally and combined with cyclization, promotes group exchange between one nitrile and the acylium ion: $RCO^+ + 2\ R^1CN \rightarrow$ cyclic 1,3,5-oxadiazinium ion $\rightarrow R^1CO^+ + R^1CN + RCN$. Isomeric 4,6-disubstituted 1,3,5-oxadiazinium ions are easily distinguished because the nitrile added second is lost first via the double retro-addition dissociation. (Int J Mass Spectrom 212 (2001) 445–454) © 2001 Elsevier Science B.V.

Keywords: Acylium ions; Nitriles; Ion–molecule reactions; Pentaquadrupole tandem mass spectrometry; Cyclization reactions

1. Introduction

Acylium ions are common and important ionic species both in solution [1,2] and in the gas phase [3–10]. In solution, when formed in situ and because of their high reactivity, solvated acylium ions are transient species, yet many stable acylium salts have been prepared and have become common reagents in organic synthesis [11]. When isolated in the diluted gas phase environment, gaseous acylium ions are often stable and long lived; hence, as for the stable acylium ion salts, gaseous acylium ions can be formed, isolated, and then employed in gas phase reactions. Recent multiple-stage mass spectrometric studies have explored systematically the intrinsic reactivity of acylium ions and demonstrated the synthetic and analytical applications of their gas phase reactions [12–25]. Gaseous acylium ions tend to

---

*Corresponding author. E-mail eberlin@iqm.unicamp.br

Dedicated to Graham (R.G. Cooks) for his continuous guidance, inspiration, and friendship and for his outstanding contributions to many fields in mass spectrometry including gas phase ion chemistry.

PII S1387-3806(01)00441-9

behave similarly to carbonyl compounds and, accordingly, they undergo ketalization with diols and analogues [12,13] and transacetalization with five- and six-membered cyclic acetals and ketals [14–19]. With seven-membered ring acetals and ketals, however, acylium ions react predominantly or exclusively by O-acylation followed by ring contraction [20]. With dienes, acylium ions undergo polar $[4+2^+]$ cycloadditions [21,22], and with epoxides, they react by O-acylation followed by ring expansion [23]. The halogen acylium ions, with the reactivity order $F–CO^+ \gg Cl–CO^+ > Br–CO^+$, promote carbonylation of benzene [24,25] and five-membered heterocyclics [25] via selective functionalization of their relatively inert C–H ring bonds.

In solution, acylium ions react via cyclization with aryl nitriles, cyanamides, carbodiimides, alkenes, and alkynes, yielding many types of heterocyclic ions [11]. As shown by Eitner and Kraft as early as 1892 [26], and as shown again, later, by Meerwein et al. [27] and Schmidt [28], two equivalents of aryl nitriles add to acylium ions to form aromatic 1,3,5-oxadiazinium ions, which are useful intermediates in the synthesis of many heterocycles [11]. Despite this rich and useful reactivity in solution, and the ready access to gaseous acylium ions, no such cyclization reactions have yet been investigated in the gas phase. Here we report on a systematic investigation using pentaquadrupole mass spectrometry [29] of the intrinsic cyclization reactivity of gaseous acylium ions with nitriles and on the formation, isolation, and characterization of the cyclic 1,3,5-oxadiazinium product ions.

2. Methods

Double- (MS^2) and triple-stage (MS^3) mass spectrometric experiments performed with an Extrel (Pittsburgh, PA) pentaquadrupole ($Q_1q_2Q_3q_4Q_5$) mass spectrometer [29,30] were used to form the gaseous acylium ions, to perform their reactions with the freshly dried nitriles, and to structurally characterize product ions. Appropriate precursors were used to form the reactant ions by 70 eV electron ionization: **1** and **3** (methyl phenyl ketone), **2** (ethyl vinyl ketone), and **4** (tetramethyl urea).

The reactions were performed by MS^2 experiments via which the acylium ion of interest was mass selected by Q_1 for further reactions in q_2 with the neutral nitrile. Ion translational energies were set to ~1 eV, as calibrated by the *m/z* 39 : 41 ratio in neutral ethylene/ionized ethylene reactions [31]. To record the product ion mass spectra, Q_5 was scanned while operating Q_3 in the broadband rf-only mode. Multiple collision conditions that caused typical beam attenuations of 50%–70% were used in q_2 so as to increase reaction yields and promote collisional quenching of both the reactant and product ions [29].

For the MS^3 experiments [32], a 1,3,5-oxadiazinium ion formed in q_2 was mass selected by Q_3 and further dissociated by 15 eV collision dissociation with argon or reacted at ~0 eV collisions with nitrogen nucleophiles in q_4 while scanning Q_5 to acquire the spectra. The 15 eV collision energies was 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} (q4) Torr, respectively.

Optimized geometries and energies of idealized conformations were obtained by theoretical calculations with no symmetry constraints, using Becke3LYP [33–35] DFT/HF hybrid functionals and 6-311+G(d,p) basis sets as implemented in Gaussian98 [36].

3. Results and Discussion

Four acylium ions (Ac^+): the acetyl cation **1**, the acrilyl cation **2**, the benzoyl cation **3**, and the dimethyl carbamyl cation **4**, and four of the most common nitriles (M), acetonitrile, propionitrile, acrylonitrile, and benzonitrile, were selected. Table 1 collects the product ion mass spectra, whereas Fig. 1 shows two of these spectra as examples.

Under the multiple-collision conditions used, two major reactions are observed: first, a proton transfer that, because of the multiple collisions, may occur either from the reactant ion (Ac^+) or product ions or

Table 1
Main products (*m/z* [relative abundance]) from the reactions of acylium ions (Ac^+) with the nitriles (M)

			$CH_3{-}C{\equiv}N$			$C_2H_5{-}C{\equiv}N$			$CH_2{=}CH{-}C{\equiv}N$			$C_6H_5{-}C{\equiv}N$		
Ion	Structure	*m/z*	MH^+ M_2H^+	MAc^+	M_2Ac^+	MH^+ M_2H^+	MAc^+	M_2Ac^+	MH^+ M_2H^+	MAc^+	M_2Ac^+	MH^+ M_2H^+	MAc^+	M_2Ac^+
1	$CH_3{-}C^+{=}O$	43	42 (22) 83 (100)	84 (4)	none	56 (18) 111 (100)	98 (12)	153 (1)	54 (11) 107 (100)	96 (26)	149 (2)	104 (3) 207 (100)	146 (3)	249 (23)
2	$CH_2{=}CH{-}C^+{=}O^a$	55	42 (35) 83 (100)	96 (28)	none	56 (89) 111 (100)	none	none	54 (8) 107 (100)	108 (23)	161 (1)	104 (8) 207 (100)	158 (12)	261 (38)
3	$Ph{-}C^+{=}O^b$	105	none	146 (3)	none	56 (4) 111 (3)	160 (12)	none	54 (4) 107 (22)	158 (3)	none	104 (2) 207 (45)	208 (36)	311 (43)
4	$(CH_3)_2N{-}C^+{=}O^a$	72	42 (1) 83 (28)	113 (1)	154 (100)	56 (2) 111 (13)	127 (3)	182 (100)	54 (1) 107 (22)	125 (2)	178 (100)	104 (2) 207 (8)	175 (4)	278 (100)

Note. MH^+ denotes the protonated nitrile; M_2H^+, the nitrile proton-bonded dimer; MAc^+ the adduct; and M_2Ac^+ the cyclic 1,3,5–oxadiazinium ions.

[a] Except for benzonitrile, water contaminating the other hygroscopic nitriles adds to the acylium ions **2** and **4** to form H_2OAc^+, which reacts in turn with the nitrile to form MH_2OAc^+ to variable extents depending on the nitrile humidity. For freshly dried nitriles, these products are minor.

[b] The main product ion when **3** reacts with the nitriles is MPh^+. Dissociation of **3** by CO loss forms Ph^+, and its subsequent addition reaction with the nitrile forms MPh^+

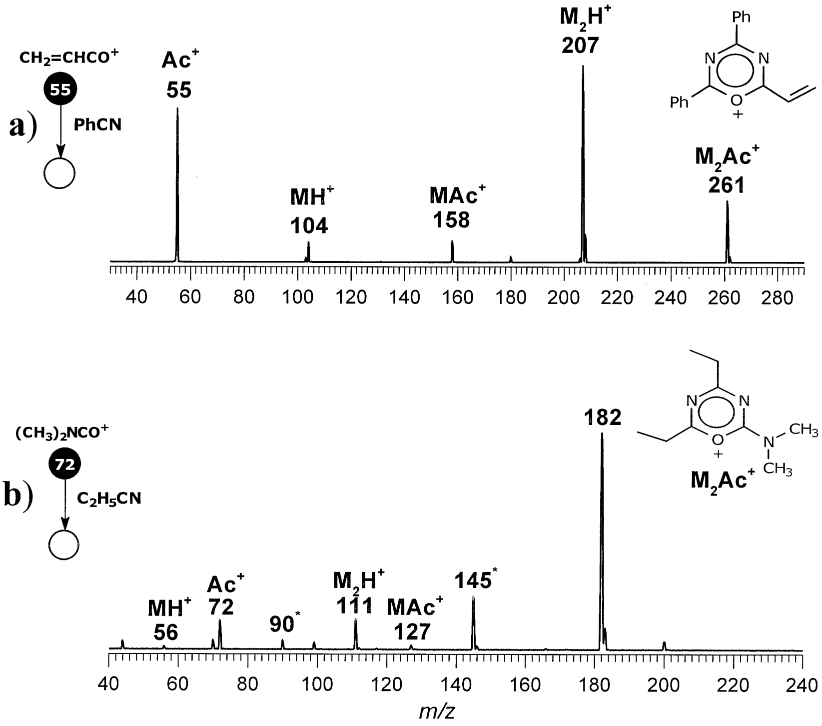
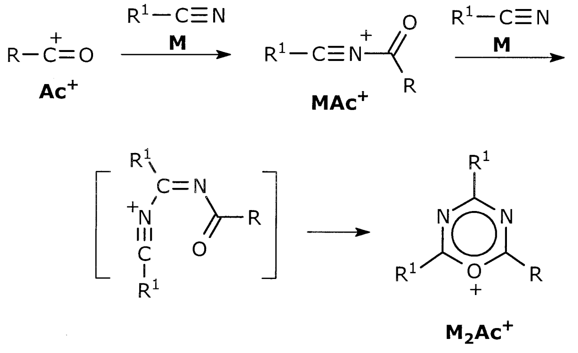


Fig. 1. Double-stage (MS^2) product ion mass spectra for reactions of (a) the acylium ion **2** with benzonitrile and (b) the acylium ion **4** with propionitrile. *M* denotes the nitrile, and Ac$^+$ the acylium ion. The marked products in (b) are formed by addition of water (a common contaminant of the hygroscopic propionitrile) to **4**, which forms *m/z* 90, and by further proprionitrile addition to *m/z* 90, which forms *m/z* 145.

from both, yielding the protonated nitrile (MH$^+$) and, subsequently, the nitrile proton-bonded dimer (M$_2$H$^+$); and, second, single-plus-double nitrile addition (Scheme 1). Single nitrile addition to the acylium ion (Ac$^+$) forms the adduct MAc$^+$, and a second nitrile addition forms the dimer M$_2$Ac$^+$, that is, the cyclic 1,3,5-oxadiazinium ion as demonstrated below.



Scheme 1.

Note that M$_2$Ac$^+$ can also be described as 3,5-diazapyrilium ions.

3.1. Cyclization reactivity of the acylium ions

As seen in Table 1, the acylium ions **1** and **2** are the least reactive toward cyclization with nitriles; both **1** and **2** react predominantly by proton transfer to form both MH$^+$ and M$_2$H$^+$, and only in reactions with benzonitrile do they form abundant dimers, M$_2$Ac$^+$. Fig. 1a shows the product ion mass spectrum for reactions of **2** with benzonitrile. The cyclic 1,3,5-oxadiazinium ion of *m/z* 261 is formed via the *N*-acylated monomer of *m/z* 158, but proton transfer that forms MH$^+$ of *m/z* 104, and mainly M$_2$H$^+$ of *m/z* 207, occurs to a greater extent. High proclivity to react by proton transfer is common for **1** and **2** because of their relatively high acidity [29]; **1** and **2**

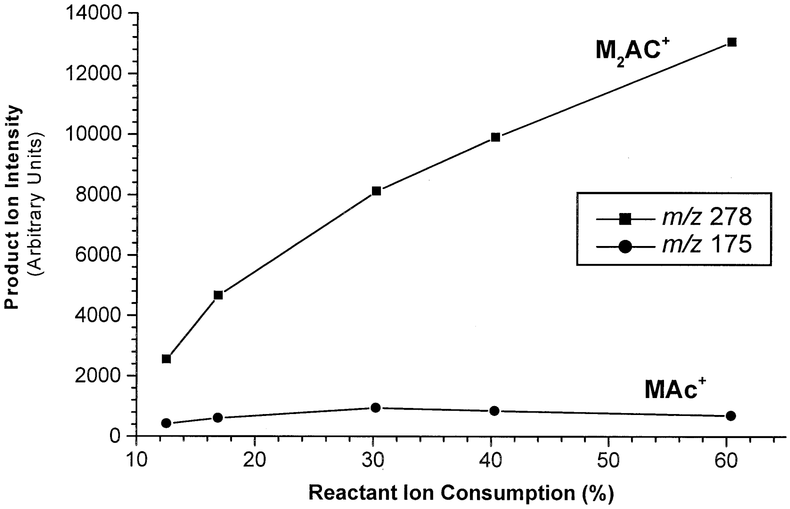


Fig. 2. Plot of the relative yields of the MAc^+ (m/z 175) and M_2Ac^+ (m/z 278) products formed in reactions of **4** with benzonitrile as a function of reactant ion consumption. Ion consumption provides an indirect but precise measurement of the relative benzonitrile pressures inside the q_2 reaction cell.

are protonated forms of ketene and 1,2-propadienone, respectively.

The benzoyl cation **3** of *m/z* 105 is much less acidic than **1** and **2** [29] but MH^+ and M_2H^+ are still formed in its reactions with the nitriles (Table 1), which indicates that proton transfer occurs mainly from product ions. As for **1** and **2**, cyclization that forms M_2Ac^+ is observed for **3** as a major reaction only when it reacts with benzonitrile. For **3** exclusively, a third reaction is often dominant; even under the low-energy collision conditions employed, **3** dissociates by CO loss to form the phenyl cation, Ph^+, and then the nitrile adds readily to Ph^+ to form relatively abundant MPh^+ adducts.

As for cyclization with nitriles, **4** is found to be by far the most reactive among the four acylium ions tested (Table 1). With the four nitriles tested, **4** reacts readily, and predominantly by cyclization via double addition, to form abundant 1,3,5-oxadiazinium ions, M_2Ac^+. Fig. 1b shows the product ion mass spectrum for reactions of **4** with propionitrile. Via the *N*-acylated acrylonitrile of *m/z* 127 (MAc^+), the cyclic 1,3,5-oxadiazinium ion of *m/z* 182 is formed to a great extent, whereas the proton transfer products of *m/z* 56 and 111 are minor. Although freshly dried nitriles were used, two additional products seem in Fig. 1b were formed by a reaction sequence initiated by addition of water (a common contaminant of hygroscopic nitriles) to **4**, which forms H_2OAc^+ of *m/z* 90, and by proprionitrile addition to H_2OAc^+, which forms MH_2OAc^+ of *m/z* 145. A similar reaction sequence was also observed for **2** in reactions with hygroscopic nitriles.

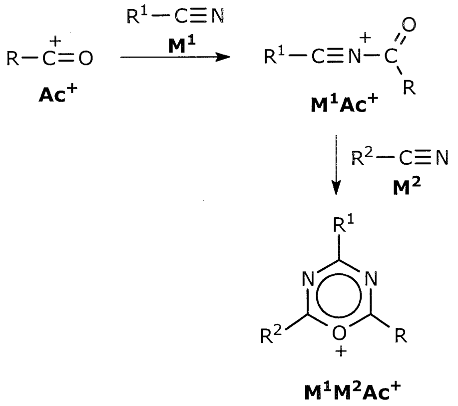
3.2. *Reactivity of MAc^+ toward a second nitrile addition*

The *N*-acylated nitriles (MAc^+) of *m/z* 158 in Fig. 1a and of *m/z* 127 in Fig. 1b are detected at much lower abundances than M_2Ac^+, which indicates high reactivity of these MAc^+ adducts towards a second nitrile addition. This high reactivity was tested by reacting **4** with benzonitrile and by plotting the yields of both MAc^+ of *m/z* 175 and M_2Ac^+ of *m/z* 278 as a function of consumption of **4** (Fig. 2). Reactant ion consumption provides an indirect but precise measurement of the relative benzonitrile pressures inside the q_2 reaction cell [29]. Even at low benzonitrile pressures under which little of **4** is consumed, M_2Ac^+ dominates, and its abundance increases rapidly and continuously with pressure. The relative abundance of

MAc^+ is always low and tends to decrease even further with higher benzonitrile pressures. These trends confirm, therefore, that the high reactivity of MAc^+ towards a second nitrile addition, as expected if one considers that cyclic, aromatic, and therefore, highly stable 1,3,5-oxadiazinium ions are formed via the second nitrile addition followed by spontaneous (see the theoretical calculation section below) cyclization.

3.3. One-pot synthesis of isomeric 4,6-disubstituted 1,3,5-oxadiazinium ions

The two-step cyclization of gaseous acylium ions via double nitrile addition provides a (selective) pathway to isomeric 4,6-disubstituted 1,3,5-oxadiazinium ions ($M^1M^2Ac^+$) via one-pot reactions with nitrile mixtures (Scheme 2).

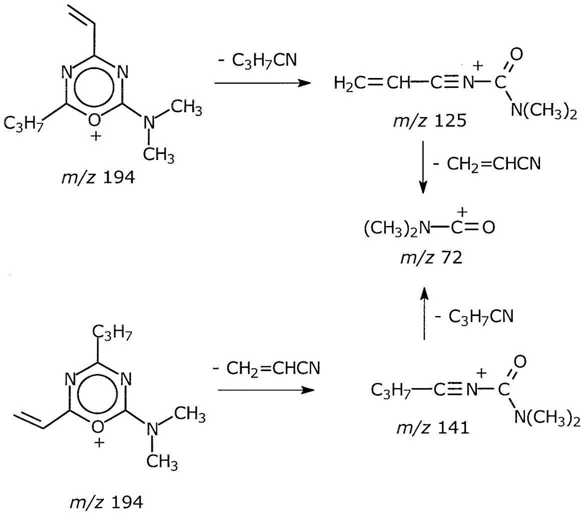


Scheme 2.

These one-pot reactions were performed for **4** with two-component mixtures of the four nitriles listed in Table 1, as well as butyronitrile, and the four expected 1,3,5-oxadiazinium ions were readily formed in all reactions. Fig. 3a illustrates the relevant portion of the resulting product ion mass spectrum for the one-pot reaction of **4** with a mixture of acrylonitrile and butyronitrile. The expected cyclic products are 4,6-divinyl (*m/z* 178), 4,6-dipropyl (*m/z* 210), and the two isomeric 4-propyl 6-vinyl and 4-vinyl 6-propyl (*m/z* 194) 2-*N*,*N*-dimethylamino 1,3,5-oxodiazinium ions, which are the major products, with the relative abundance of the isomeric $M^1M^2Ac^+$ products of *m/z* 194 being, as expected, nearly twice as great.

3.4. Collision-induced dissociation (CID) of the 1,3,5-oxadiazinium ions

Fig. 3b and 3d displays triple-stage CID mass spectra of two cyclic 1,3,5-oxadiazinium ions. Those of *m/z* 178 formed by double addition of acrylonitrile to **4** dissociate exclusively to re-form, first, the monomer (*m/z* 125) by neutral acrylonitrile loss and, subsequently, the reactant acylium ion (*m/z* 72) by a second acrylonitrile loss (Fig. 3b). Similarly, those of *m/z* 210 (Fig. 3d) formed by double addition of butyronitrile to **4** dissociate exclusively to re-form, first, the monomer (*m/z* 141) and, subsequently, the reactant acylium ion (*m/z* 72). But the isomeric 4-propyl 6-vinyl and 4-vinyl 6-propyl disubstituted 1,3,5-oxadiazinium ions of *m/z* 194 are expected to dissociate diversely by retro double addition because the nitrile added second should be lost first (Scheme 3). Accordingly, the two expected monomers of *m/z* 141 and 125 are detected in their CID mass spectrum (Fig. 3c).



Scheme 3.

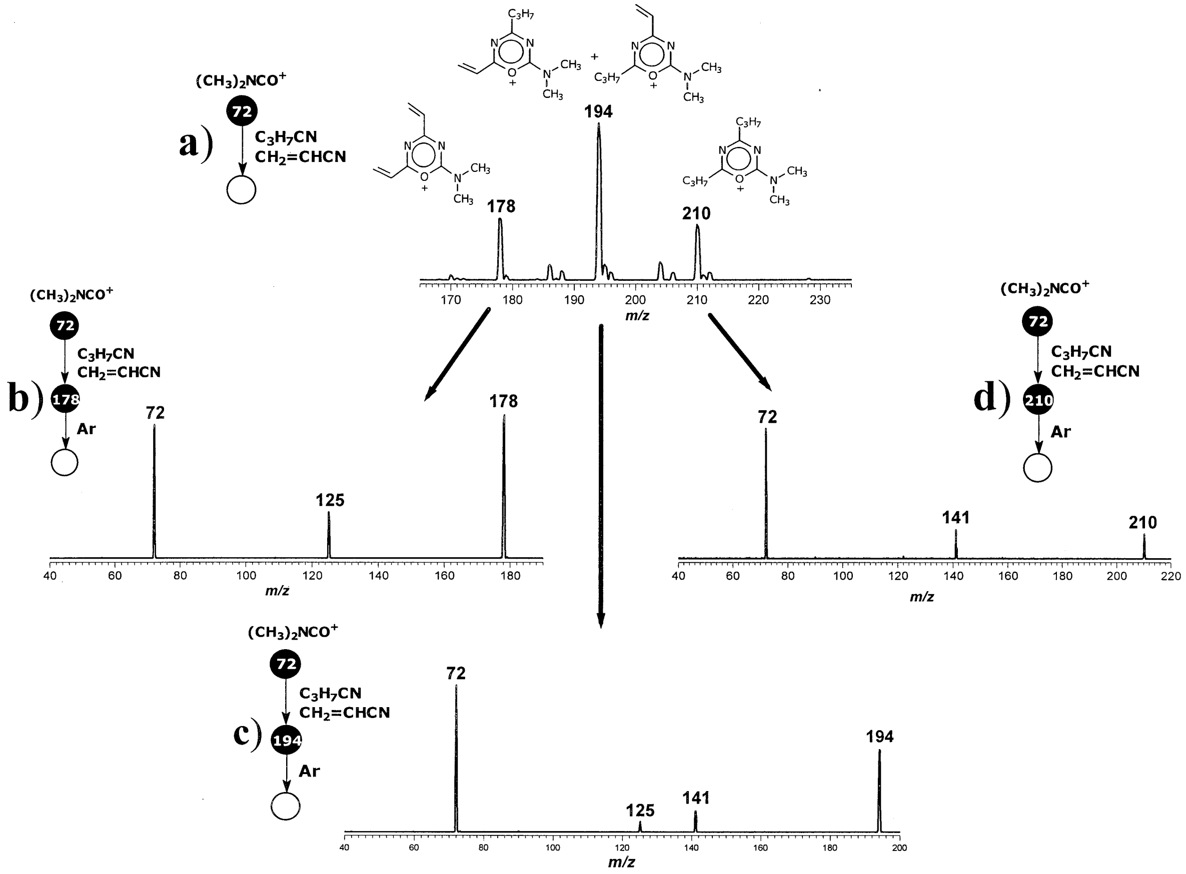


Fig. 3. (a) A segment of the double-stage (MS^2) product ion mass spectrum for reactions of the acylium ion **4** with a mixture of acrylonitrile and benzonitrile. Triple-stage (MS^3) sequential collision-induced dissociation product ion mass spectra of the cyclic 1,3,5-oxadiazinium product ions of (b) *m/z* 178 (c) *m/z* 194, and (d) *m/z* 210.

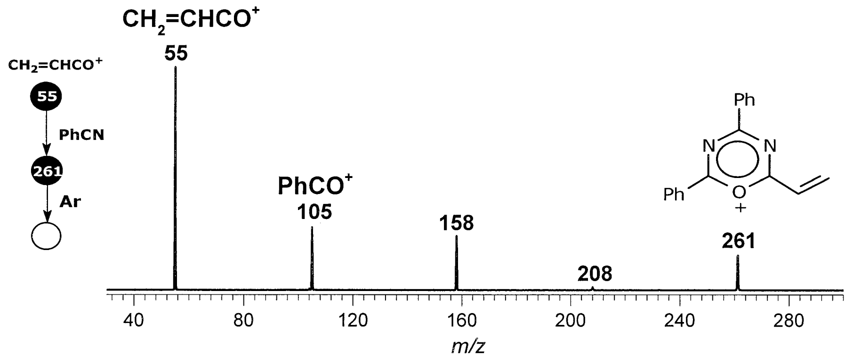


Fig. 4. Triple-stage (MS^3) sequential collision-induced dissociation product ion mass spectrum of the cyclic 2-vinyl 4,6-diphenyl 1,3,5-oxadiazinium ion of *m/z* 261 formed in reactions of **2** with benzonitrile.

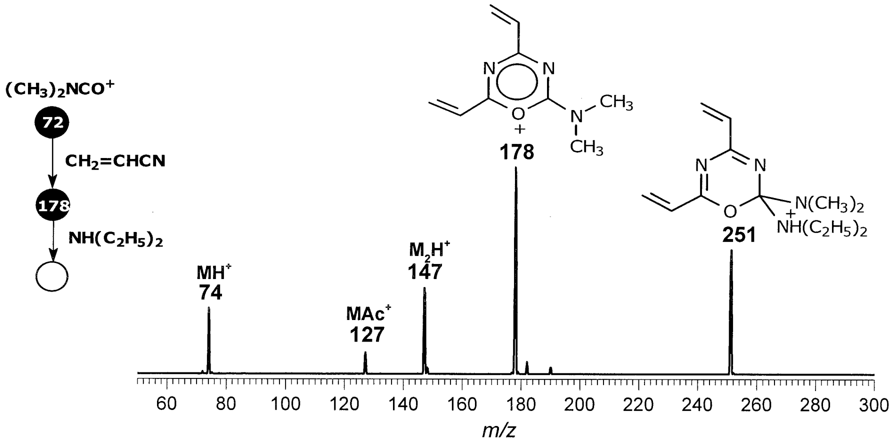
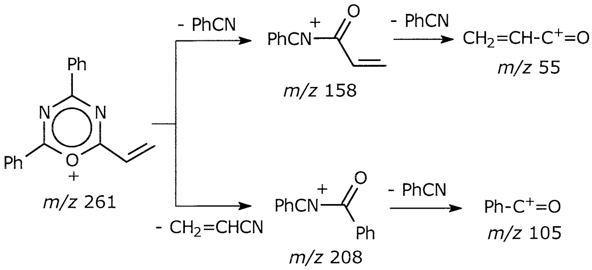


Fig. 5. Triple-stage (MS^3) sequential product ion mass spectrum for reaction in q_4 with diethylamine of the cyclic 1,3,5-oxadiazinium ion of *m/z* 178 formed in q_2 by the reaction of **4** with acrylonitrile.

The spectrum of Fig. 4 is also structurally elucidative. Whereas all 1,3,5-oxadiazinium ions formed from **4** dissociate exclusively by double retro-addition to re-form the reactant ion **4**, as exemplified in Fig. 3b and 3d, the 1,3,5-oxadiazinium ion of *m/z* 261 formed by double addition of benzonitrile to **2** (Fig. 1a) dissociates to form both the reactant ion **2** of *m/z* 55 and the benzoyl cation **3** of *m/z* 105. Two acylium ions are formed because the symmetry of the 1,3,5-oxadiazinium ring, and the presence of different substituents at the 2- and 4-ring positions, allows two competitive dissociation pathways (Scheme 4): either double retro-addition that re-forms the reactant acylium ion **2** of *m/z* 55 or an analogous dissociation pathway that promotes, both formally and combined with cyclization, unique group exchange between benzonitrile and the acylium ion **2**, yielding acrylonitrile and $PhCO^+$ (**3**). Similar competitive dissociations that yield both **1** and **3** are also observed for the 2-methyl 4,6-diphenyl 1,3,5-oxadiazinium ion of *m/z* 249 (spectrum not shown) formed by cyclization of **1** with benzonitrile (Table 1). Note that the group-exchange dissociation can only be rationalized with the intermediacy of *cyclic* 1,3,5-oxadiazinium ions, which provides evidence for cyclization.



Scheme 4.

3.5. Nucleophile addition to 1,3,5-oxadiazinium ions

In solution, the triphenyl 1,3,5-oxadiazinium ion formed by cyclization of **3** with benzonitrile is known to react with nucleophiles, and nitrogen nucleophiles in particular, to yield a variety of heterocyclic compounds after a series of addition, intermolecular proton transfer, and elimination reactions [11]. The gaseous 1,3,5-oxadiazinium ion of *m/z* 178 formed by cyclization of **4** with (two molecules of) acrylonitrile was, therefore, selected and reacted in MS^3 experiments with four nitrogen nucleophiles: *N*,*N*-dimethyl hydrazine, diethyl amine (Fig. 5), pyridine, and pyrrolidine. Addition occurs readily for the four nucleophiles, but no product ion equivalent to those formed in solution were observed. Perhaps the reaction sequences observed in solution involving intermolecular proton transfer and equilibrium reactions are hampered in the gas phase because of too-energetic

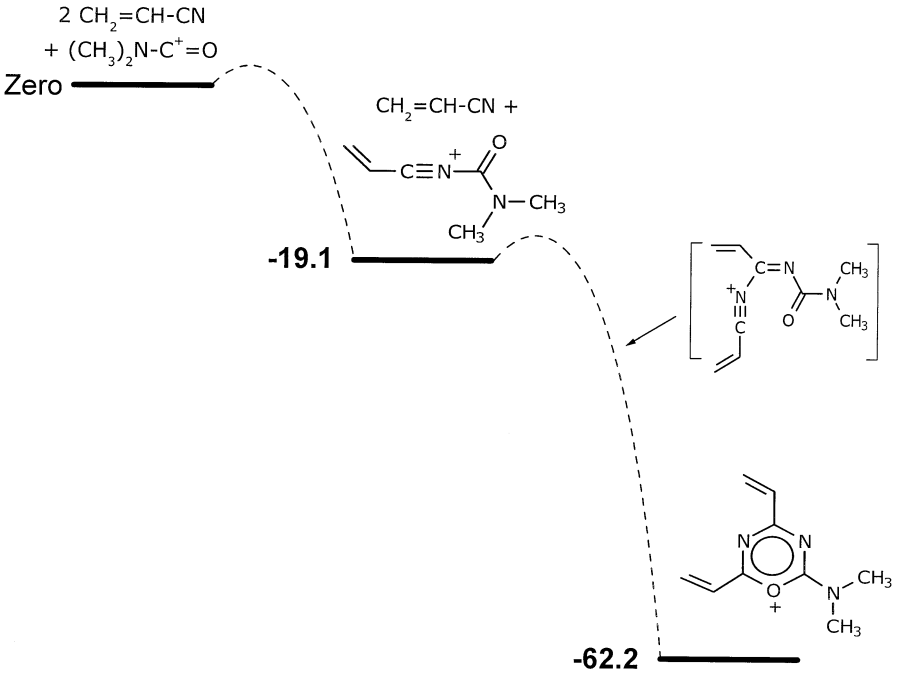


Fig. 6. Becke3LYP/6-311+G(d,p) potential energy surface diagram for the reaction of **4** with acrylonitrile. Reaction barriers were not estimated. The acyclic dimer formed by double acrylonitrile addition (see Scheme 1) is unstable and collapses with no energy barrier to the cyclic 1,3,5-oxadiazinium ion during geometry optimization. The energies of the species are, in hartrees: **4** (−247.68463), acrylonitrile (−170.88288), N-acylated acrylonitrile (−418.59800), and the 1,3,5-oxadiazinium ion (−589.54960).

intramolecular proton transfer reactions and/or kinetic constrains.

3.6. Theoretical calculations: reaction enthalpies

Fig. 6 shows a potential energy surface diagram for a model reaction, that of **4** with (two molecules of) acrylonitrile. Single addition occurs favorably via a −19.1 kcal/mol exothermic *N*-acylation reaction. A second acrylonitrile addition is even more thermodynamically favored, being overall exothermic by −62.2 kcal/mol; it leads to an unstable acyclic dimer (see Scheme 1) that, during structure optimization, collapses with no energy barrier to the cyclic 1,3,5-oxadiazinium ion. Hence, the acyclic dimer corresponds merely to a point on the energy surface that connects the monomer to the cyclic 1,3,5-oxadiazinium ion. The higher exothermicity of the second nitrile addition that yields the aromatic and highly stable 1,3,5-oxadiazinium ions accounts, therefore, for the observed high reactivity of MAc$^+$, as discussed previously.

4. Conclusion

Similar to the behavior in solution, and as demonstrated here for **1**–**4** and benzonitrile, gaseous acylium ions react readily with aryl nitriles by cyclization via double addition to form aromatic, highly stable, and cyclic 1,3,5-oxadiazinium ions. Aryl nitriles are more reactive probably because both the *N*-acylated nitrile intermediates and the final cyclic 1,3,5-oxadiazinium ions are stabilized by charge delocalization through the aromatic ring. Cyclization of acylium ions with aliphatic nitriles, as demonstrated here for acetonitrile, propionitrile, and acrylonitrile, is less general and occurs readily only for **4**, by far the least acidic and most reactive acylium ion tested. Because cyclization occurs via sequential double nitrile addition, isomeric 4,6-disubstituted 1,3,5-oxadiazinium ions can be formed by one-pot reactions of reactive acylium ions with two-component nitrile mixtures.

The symmetry of the 1,3,5-oxadiazinium ring allows two alternative dissociation pathways: either double retro-addition that re-forms the reactant acylium ion or an analogous dissociation that promotes, both formally and combined with cyclization, unique group exchange between one nitrile and the acylium ion, a process summarized as follow: $RCO^+ + 2\ R^1CN \rightarrow$ cyclic 1,3,5-oxadiazinium ion $\rightarrow R^1CO^+ + R^1CN + RCN$. Depending on the substituents at the 2- and 6-ring positions, these dissociations may compete or dominate over each other, whereas the group-exchange dissociation proves that cyclic 1,3,5-oxadiazinium ions are formed. Isomeric 1,3,5-oxadiazinium ions with different 4,6-substituents are easily distinguished by CID because, via the double retro-addition dissociation, the nitrile added second is lost first.

Acknowledgements

This work has been supported by the Research Support Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq).

References

[1] G.A. Olah, A. Gramain, A.M. White, in Carbonium Ions Vol. 5, G.A. Olah, P. von R. Schleyer, (Eds.), Wiley Interscience, New York 1976, p. 2084.

[2] G.A. Olah, K.K. Laali, Q. Wang, G.K.S. Prakash. Onium Ions, Wiley, New York 1998.,

[3] D.A. Chatfield, M.M. Bursey, J. Am. Chem. Soc. 98 (1976) 6492.

[4] R.H. Staley, R.D. Wieting, J.L. Beauchamp, J. Am. Chem. Soc. 99 (1977) 5964.

[5] C. Sparapani, M. Speranza, J. Am. Chem. Soc. 102 (1980) 3120.

[6] M. Attiná, F. Cacace, J. Am. Chem. Soc. 105 (1983) 1122.

[7] M.C. Caserio, J.K. Kim, J. Am. Chem. Soc. 105 (1983) 6896.

[8] N.A. Rahman, C.L. Fisher, M.C. Caserio, Org. Mass Spectrom. 23 (1988) 517.

[9] T. Kotiaho, M.N. Eberlin, B.J. Shay, R.G. Cooks, J. Am. Chem. Soc. 115 (1993) 1004.

[10] C.S. Creaser, B.L. Wiliamson, J. Chem. Soc. Perkin Trans. 2 (1996) 427.

[11] M. Al-Talib, H. Tashtoush, Org. Prep. Proceed. Int. 22 (1990) 1.

[12] L.A.B. Moraes, R.S. Pimpim, M.N. Eberlin, J. Org. Chem. 61 (1996) 8726.

[13] L.A.B. Moares, M.N. Eberlin, J. Am. Soc. Mass Spectrom. 12 (2001) 150.

[14] M.N. Eberlin, R.G. Cooks, Org. Mass Spectrom. 28 (1993) 679.

[15] L.A.B. Moraes, F.C. Gozzo, M.N. Eberlin, P. Vainiotalo, J. Org. Chem. 62 (1997) 5096.

[16] M.C. Carvalho, V.F. Juliano, C. Kascheres, M.N. Eberlin, J. Chem. Soc. Perkin Trans. 2 (1997) 2347.

[17] L.A.B. Moraes, M.N. Eberlin, J. Am. Chem. Soc. 120 (1998) 11136.

[18] R. Sparrapan, M.A. Mendes, M.N. Eberlin, J. Mass Spectrom. 35 (2000) 189.

[19] L.A.B. Moraes, M.A. Mendes, R. Sparrapan, M.N. Eberlin, J. Am. Soc. Mass Spectrom. 12 (2001) 14.

[20] L.A.B. Moares, T. Kotiaho, M.N. Eberlin, J. Mass Spectrom. 34 (1999) 670.

[21] M.N. Eberlin, T.K. Majumdar, R.G. Cooks, J. Am. Chem. Soc. 114 (1992) 2884.

[22] M.N. Eberlin, R.G. Cooks, J. Am. Chem. Soc. 115 (1993) 9226.

[23] L.A.B. Moraes, M.N. Eberlin, Chem. Eur. J. 6 (2000) 897.

[24] F. Grandinetti, F. Pepi, A. Ricci, Chem. Eur. J. 2 (1996) 495.

[25] L.A.B. Moraes, M.A. Mendes, R. Sparrapan, M.N. Eberlin, J. Am. Soc. Mass Spectrom. 12 (2001) 14.

[26] P. Eitner, F. Kraft, Chem. Ber. 25 (1892) 2267.

[27] H. Meerwein, H. Laasch, P. Mersch, J. Spille, Chem. Ber. 89 (1956) 209.

[28] R.R. Schmidt, Chem. Ber. 98 (1965) 334.

[29] M.N. Eberlin, Mass Spectrom. Rev. 16 (1997) 113.

[30] V.F. Juliano, C. Kascheres, F.C. Gozzo, M.N. Eberlin, C.L. Lago, Anal. Chem. 68 (1996) 1328.

[31] T.O. Tiernan, J.O. Futrell, J. Phys. Chem. 72 (1968) 3080.

[32] J.C. Schwartz, A.P. Wade, C.G. Enke, R.G. Cooks, Anal. Chem. 62 (1990) 1809.

[33] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[34] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.

[35] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[36] Gaussian 98, Revision A.6., M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K.J.B. Raghavachari, J. Foresman, J.V. Cioslowski, B. Ortiz, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.