J. Org. Chem. **2000,** *65,* 964−968

$C_5H_7O_2^+$ Ions: The Correlation between Their Thermochemistry in Acidic Solution and Their Chemistry in the Gas Phase

Gregorio Asensio,*,† Miguel A. Miranda,‡ María J. Sabater,‡ Julia Pérez-Prieto,†
Antonio Simón-Fuentes,† and Rossella Mello†

*Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, E-46100 Burjassot,
Valencia, Spain, and Departamento de Química, Universidad Politécnica de Valencia, Apdo. 22012,
E-46071-Valencia, Spain*

Received July 1, 1999

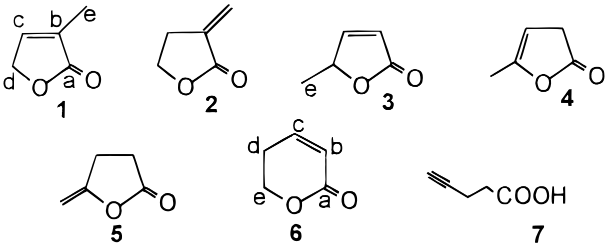
Each of a series of $C_5H_6O_2$ isomeric carboxylic acid and unsaturated lactones (**1**−**7**) was protonated in both concentrated sulfuric acid and trifluoromethanesulfonic acid. The thermally induced transformations of the protonated species were then studied over a temperature range of −30 to +160 °C. In the case of α,*β*-unsaturated lactones, protonation took place on the carbonyl oxygen and gave the corresponding stable O-protonated species. Conversely, unconjugated lactones and acetylenic acid **7** were converted even at low temperature into the diprotonated ketoacid $\mathbf{8H_2o}^{+2}$ by the acid-catalyzed addition of water to the C-protonated precursor. Upon being heated at 160 °C, this acid gave protonated 1,3-cyclopentanedione. In the absence of water, decarbonylation followed by polymerization was observed in lactones **4** and **5**. The CIMS spectra of compounds **1**−**7** were recorded using methane, ammonia, and moist air as reagent gases to determine the correlation between the fragmentation routes in the gas phase and the transformations observed in solution. Ammonia and moist air enabled us to determine the different proton affinities of these compounds. The data obtained in strong acids were used to assign reasonable structures to the gas-phase ions.

Introduction

In previous papers in this series,[1,2] we studied the protonation of carbonyl compounds in strong acid medium, the heat-induced transformations of the ionic species involved, and the correlation between the thermochemistry in strong acid solution and the chemistry in the gas phase as determined by recording the chemical ionization mass spectra (CIMS) of the corresponding precursors. These correlations have been useful, since they allow us to assign reasonable structures to the fragments produced in mass spectrometry based on the structures of the ions characterized by NMR in the thermochemistry of the corresponding precursors in solution under strong acid conditions. Thus, identification of the ions present in solution also enables us to determine the main fragmentation pathways observed by CIMS, which in turns enables us to predict the fate of the same ions in solution.[3]

We report here the results obtained by our method for a group of $C_5H_7O_2^+$ ions resulting from the protonation of unsaturated lactones **1**−**6** and the open-chain acetylenic acid **7** carried out either in 96% sulfuric acid or trifluoromethane sulfonic acid (TFMSA) in a temperature range of −30 to +160 °C.

Chart 1



Results and Discussion

Protonation of Carbonyl Derivatives 1−7. The protonation at room temperature of the conjugated lactones[4] **1**, **2**, **3**, and **6** with sulfuric acid or TFMSA gave the corresponding stable O-protonated species $\mathbf{1Ho}^+$, $\mathbf{2Ho}^+$, $\mathbf{3Ho}^+$, and $\mathbf{6Ho}^+$, respectively, which were characterized by ^1H and ^{13}C NMR (see Table 1). The observed deshielding of the carbonyl carbon (ca. 14.5 ppm) agrees well with the literature data for other O-protonated carbonyl compounds.[1,2] As expected, in these α,*β*-unsaturated lactones a parallel deshielding of the *β*-carbon (ca. 17 ppm) associated with the O-protonation process was observed due to conjugation with the protonated carbonyl group. Note the deshielding of the terminal methylene carbon atom (Ce) in ion $\mathbf{2Ho}^+$. The positive charge is further delocalized due to participation of the ether-type oxygen lone pair in oxonium-like resonance structures. This results in the downfield displacement of the signal of the *C*−O carbon atom in the ^{13}C NMR spectra of compounds **1**, **2**, **3**, and **6** due to the electron-withdrawing effect of the oxygen. The observation of O-protonated species was not possible even at low temperature (−5 °C for sulfuric acid and −30 °C for TFMSA) in the case of unconjugated carbonyl compounds. Therefore, *γ*-lactones

---

* To whom correspondence should be addressed.

† Universidad de Valencia.

‡ Universidad Politécnica de Valencia.

(1) Amat, A. M.; Asensio, G.; Castelló, M. J.; Miranda, M. A.; Simón-Fuentes, A. *J. Org. Chem.* **1987**, *52*, 4790−4792.

(2) Asensio, G.; Miranda, M. A.; Pérez-Prieto, J.; Sabater, M. J.; Simón-Fuentes, A. *J. Org. Chem.* **1992**, *57*, 6202−6206.

(3) Asensio, G.; Miranda, M. A.; Pérez-Prieto, J.; Sabater, M. J.; Simón-Fuentes, A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1146.

(4) Olah, G. A.; Ku, A. T. *J. Org. Chem.* **1970**, *35*, 3916. (b) Olah, G. A.; White, A. M.; O'Brien, D. H. *Chem. Rev.* **1970**, *70*, 561. (c) Deno, N. C.; Pittman, C. U., Jr.; Wisotsky, M. J. *J. Am. Chem. Soc.* **1964**, *107*, 818.

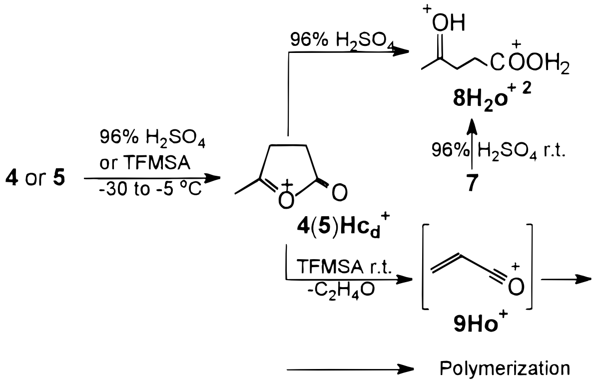
10.1021/jo991056i CCC: $19.00

Table 1. ^{13}C NMR Data for Selected Protonated Species

	δ_C (ppm)[a]				$^1J_{C-H}$ (Hz)[b]			
	1Ho$^+$	**2Ho$^+$**	**3Ho$^+$**	**6Ho$^+$**	**1Ho$^+$**	**2Ho$^+$**	**3Ho$^+$**	**6Ho$^+$**
C_a	189.3	185.6	187.4	179.3				
	(14.5)[c]	(14.2)	(14.5)	(15.3)				
C_b	129.5	131.8	117.8	115.3			193.4	182.2
	(−0.4)[c]	(−3.4)	(−2.7)	(−5.8)			(11.7)	(18.0)
C_c	163.6	26.7	173.6	165.7	201.5	139.8	187.8	171.7
	(18.7)[c]	(−1.1)	(15.9)	(18.0)		(7.1)	(19.0)	(9.5)
C_d	87.1	80.9	95.4	24.4	172.7	161.3	155.1	135.9
	(17.1)[c]	(15.1)	(16.0)	(0.1)		(8.3)	(6.3)	(11.4)
C_e	9.4	139.7	15.5	74.5	131.8	166.7	133.0	156.9
	(−1.3)[c]	(16.9)	(−2.8)	(7.5)		(5.1)	(4.7)	(7.3)

[a] In parentheses: $\Delta\delta^{13}C = \delta^{13}C$ (in spectrum of ion) − $\delta^{13}C$ (in spectrum of uncharged precursor). [b] In parentheses: $\Delta J_{C-H} = J_{C-H}$ (in spectrum of ion) − J_{C-H} (in spectrum of uncharged precursor). [c] See ref 12.

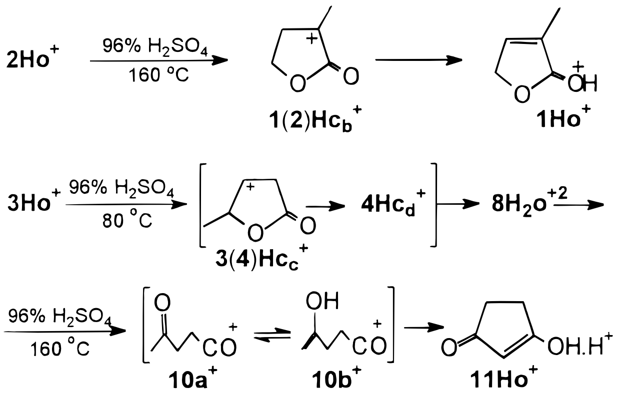
Scheme 1



4 and **5** and the open-chain acetylenic acid **7** were converted under these conditions into the diprotonated ketoacid **8H$_2$o**$^{+2}$. This transformation is easily understood if we consider the presence of water in 96% sulfuric acid; the acid-catalyzed addition of water to compounds **4**, **5**, and **7** (see Scheme 1) is likely to occur under these conditions. C-Protonation will readily take place in the case of lactones **4** and **5**, since it results in the formation of the oxonium ion **4(5)Hc$_d$**$^+$ due to the presence of the lactone oxygen bonded to the positively charged carbon. In contrast, the activation energy for C-protonation of conjugated lactones **1**, **2**, **3**, and **6** will be much higher, since the resulting carbocation is destabilized by the neighboring carbonyl group.[5] This could explain why oxygen protonation is observed at room temperature only in conjugated lactones. We should note that lactones **4** and **5** gave a polymer in trifluoromethanesulfonic acid, probably due to the tendency of terminal double bonds to polymerize under acid catalysis and also to the very low water content in this acid. A suitable pathway for the polymerization would be the ring opening of the C-protonated ion **4(5)Hc$_d$**$^+$ followed by the loss of acetaldehyde to give ion **9Ho**$^+$ (see Scheme 1).

Thermal Transformations of Protonated Species $C_5H_7O_2^+$. To determine the effect of temperature, O-protonated ions $C_5H_7O_2^+$ were heated in 96% sulfuric acid first at 60 °C and then at 160 °C, and their evolution was followed by ^1H and ^{13}C NMR. O-Protonated **1Ho**$^+$,**2Ho**$^+$, and **3Ho**$^+$ remained unchanged at 60 °C for several hours. Ion **1Ho**$^+$ was stable under these conditions even at 160 °C. Under similar conditions, ion **2Ho**$^+$ was converted into O-protonated 3-methyl-2(5*H*)-furanone (**1Ho**$^+$) by isomerization of the exocyclic double bond through the intermediate **1(2)Hc$_b$**$^+$ ion (see Scheme 2). The heating of **3Ho**$^+$ at 80 °C gave rise to its slow conversion into the diprotonated ketoacid **8H$_2$o**$^{+2}$. This is easily understood by 1,2-hydrogen shift from the C-protonated species **3Hc$_c$**$^+$ to the more stable oxonium ion **4Hc$_d$**$^+$, which undergoes water-promoted ring opening. At 160 °C, the protonated ketoacid **8H$_2$o**$^{+2}$ was converted into the protonated cyclic ketoenol **11Ho**$^+$. The enolization of **10a**$^+$ to **10b**$^+$ will proceed most probably via protonation of the carbonyl oxygen followed by deprotonation of the methyl group (see Scheme 2). Protonated carboxylic acids undergo the loss of water at this temperature to give the corresponding acylium ion.[6] For this reason, the route proposed in Scheme 2 is the most likely to explain the observed acylation of the enolic terminal carbon. The structure of ions **8H$_2$o**$^{+2}$ and **11Ho**$^+$ was ascertained upon protonation of the parent ketoacid and diketone, respectively, under similar conditions.

Scheme 2



The methyl substitution at the α-carbon does not enable the isomerization of ion **1(2)Hc$_b$**$^+$ to the corresponding oxonium ion **1(2)Hc$_d$**$^+$, and for this reason compounds **1** and **2** do not undergo the acid-promoted thermal ring opening reaction found in *γ*-lactones **4** and **5**. Unsubstituted 2(5*H*)-furanone (**12**) was stable under our standard conditions and gave polymeric materials by heating at 160 °C for a long period of time. This behavior is consistent with the transformations described above due to the lack of *γ*-methyl substitution in the five-membered ring of **12**.

δ-Lactone **6** was stable in 96% sulfuric acid at 60 °C, but gave **11Ho**$^+$ at 160 °C, probably through a bicyclic oxonium intermediate **13Hc**$^+$ formed by trapping of the secondary cation resulting from a 1,2-hydrogen shift after C-protonation of **6** at the α-carbon, by the lactone oxygen lone pair, as depicted in Scheme 3.

Transformations of the Ions 1Ho$^+$−7Ho$^+$ in the Gas Phase versus Thermally Induced Transformations in Acid Solution. The neutral species **1**−**7** were subjected to comparative experiments with chemical ionization mass spectrometry (CIMS)[7] using methane, ammonia, or moist air (containing 6.7 g/m^3 water) as the reagent gas. According to proton affinity−activation energy correlations, the carbonyl oxygen is the thermodynamically favored protonation site.[8]

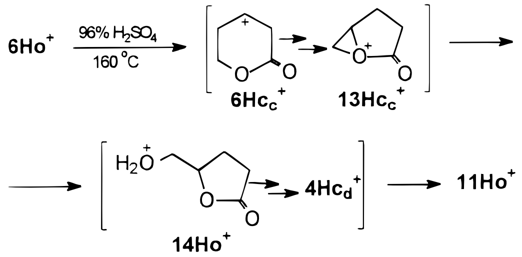
---

(5) Amat, A. M.; Asensio, G.; Castelló, M. J.; Miranda, M. A.; Simón-Fuentes, A. *Tetrahedron* **1987**, *43*, 905.

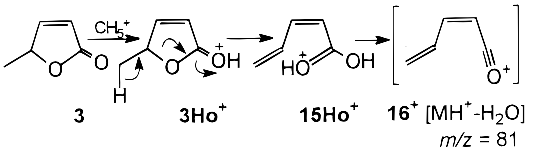
(6) Amat, A. M.; Asensio, G.; Miranda, M. A.; Sabater, M. J.; Simón-Fuentes, A. *J. Org. Chem.* **1988**, *53*, 5480−5484.

(7) Benoit, F. M.; Harrison, A. G. *J. Am. Chem. Soc.* **1977**, *99*, 3980.

Scheme 3



Scheme 4



Chemical Ionization with Methane. All of the compounds with the exception of **7** gave [MH^+] as base peak. Since this ion was very stable in all cases, weak fragmentation was observed. The main fragmentation pathway for [MH^+] was the loss of water to give the ion [$MH^+ - H_2O$] ($m/z = 81$). Different dehydration patterns can be envisaged depending on the conjugated or unconjugated nature of the double bond relative to the carbonyl group. In the case of conjugated lactones **1**, **2**, **3**, and **6**, dehydration would be preceded by ring opening and would eventually lead to the formation of an acylium ion **16**$^+$. As an example, the reaction sequence for compound **3** is shown in Scheme 4.

Accordingly, the loss of water requires proton abstraction from a primary carbon or a secondary carbon atom for compounds **1** and **3** or **2** and **6**, respectively. Comparison of the relative intensities of the peaks corresponding to the [$MH^+ - H_2O$] ions (see Table 2) shows the greater tendency for the abstraction of the proton from the more substituted carbon. The unconjugated lactones **4** and **5** do not show an apparently feasible pathway for dehydration to give an acylium ion, since a vinylic carbenium ion should be involved. However, in this case, a cyclic oxonium ion **17**$^+$ [$MH^+ - H_2O$] can be generated via an energetically less-favorable pathway (see Scheme 5). Saturated lactones[1] also show the dehydration pattern described above for their unsaturated counterparts, most probably yielding the corresponding acylium ion, as in the case of conjugated lactones **1**, **2**, **3**, and **6**. Note that carboxylic acid esters, the open-chain analogues of the lactone functionality, do not show a loss of water in the CIMS spectrum.[8]

Another important fragmentation gives rise to the ion set **19**$^+$ ($m/z = 71$). This fragmentation is most important for compounds **4** and **5**, which bear the lactone ring oxygen bonded to a vinylic carbon, and corresponds to the loss of CO (as determined by HRMS) from **18Hc**$^+$ through the formation of the intermediate ion **4**(**5**)**Hc**$_d^+$. This ion was an intermediate in the ring opening of the parent lactones in solution, but undergoes decarbonylation in the gas phase in the absence of water. The suggested fragmentation pattern is shown in Scheme 6.

In the case of lactones **1**, **2**, **3**, and **6**, there is no trivial pathway for the decarbonylation process, but the loss of ethylene, ascertained by HRMS, is readily explained through the formation of the corresponding protonated dienoic carboxylic acids **15Ho**$^+$ and **20Ho**$^+$ ions, as shown in Scheme 7. Ion **15Ho**$^+$ is a common precursor that was previously postulated in the formation of [$MH^+ - H_2O$] ions **16**$^+$ (see Scheme 4).

The last significant fragmentation occurs with the loss of CH_2O to give the [$MH^+ - CH_2O$] (**21H**$^+$) $m/z = 69$ and [$M^{+\cdot} - CH_2O$] (**22**$^{+\cdot}$) $m/z = 68$ ions. The former ion comes from the corresponding protonated species and the latter comes from a [$M^{+\cdot}$] ion resulting from a charge-transfer process. The [$MH^+ - CH_2O$] ion is very intense for compound **1**. Since the substitution patterns of compounds **1** and **2** are the same, it is noteworthy that lactone **2** does not show this type of fragmentation. However, if we assume that the CH_2O fragment is lost by a O-protonated precursor, the different behavior of these two lactones can be easily understood in terms of the fragmentation pattern shown for **1Ho**$^+$ in Scheme 8. Obviously, ion **2Ho**$^+$ cannot follow a similar path.

The ion set **22**$^{+\cdot}$ and **23**$^{+\cdot}$ [$M^{+\cdot} - CH_2O$] is observed in the case of lactones **2** and **6**. In both cases, the allylic nature of the radical involved will favor the proposed fragmentation. On the other hand, a similar rearrangement for **1o**$^{+\cdot}$ or **3o**$^{+\cdot}$ should produce vinyl radicals and is therefore energetically less favorable. In contrast, compounds **4** and **5**, due to the position of the C=C double bond will give rise to stable [$M^{+\cdot}$] ions, and this fragmentation is not observed. In fact, radical ions **4**$^{+\cdot}$ and **5**$^{+\cdot}$ $m/z = 98$ are important peaks in the CIMS spectra of these unconjugated lactones.

With methane as a reagent gas, protonated carboxylic acid **7** gives rise to several fragments of noticeable intensity. A suitable fragmentation pattern is depicted in Scheme 9. The base peak [$MH^+ - C_2H_4$] (**26Ho**$^+$) $m/z = 71$ is formed directly from the [MH^+] ion by loss of ethylene via an intramolecular cycloaddition/cycloreversion reaction as ascertained by B^2/E linked scans (see Experimental Section). The fate of **7Ho**$^+$ in solution and in the gas-phase cannot be compared, since water is not excluded in the acid solution, and this results in hydration of the triple bond, a process which does not have a parallel in the gas phase (Scheme 9).

Chemical Ionization with Ammonia and Moist Air. These reagent gases were used to achieve mass spectrometer conditions resembling those of thermochemistry in acid solution. In all cases, the CI spectra with ammonia showed the [MNH_4^+] ion $m/z = 116$ as the base peak and only selective fragmentation. The losses of water, carbon monoxide, and ethylene are practically suppressed under these less energetic conditions. Protonated ammonia efficiently transfers the proton to unsaturated lactones and, consequently, gives a significant [MH^+] ($m/z = 99$) ion in all cases (see Table 2), which shows the high proton affinity of these compounds.[9] It is noteworthy that the molecular ion [$M^{+\cdot}$] $m/z = 98$ shows greater intensity than the protonated molecule [MH^+] for compounds **4** and **5**. This indicates that the charge exchange reaction with ammonia has lower exothermicity than that with methane, which gives a molecular ion that is less prone to undergo fragmentation. Interestingly, the most significant fragmentation in the spectra with ammonia is the loss of CH_2O. In the case of compound **1**, this gives rise to the fragment ion [$MH^+ - CH_2O$] (**21H**$^+$)

---

[8] Harrison, A. G. In *Chemical Ionization Mass Spectrometry*, 2nd ed.; CRC Press: Boca Raton, 1992.

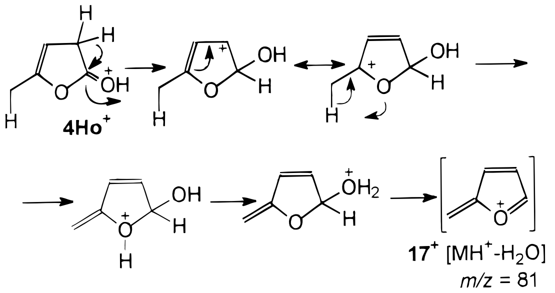
[9] Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 7705.

Table 2. Relative Intensities (%) of the Most Significant Peaks in the CI Mass Spectra of Compounds $C_5H_6O_2$ (1−7) with Methane and Ammonia as Reagent Gas

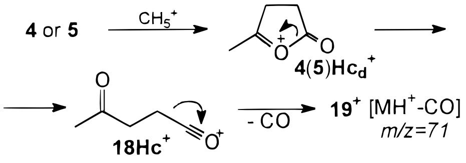
		peak intensity (%)[a] and $[M^{+\cdot}]/[MH^+]$ ratio[b] for compound						
m/z	ion	**1**	**2**	**3**	**4**	**5**	**6**	**7**
116	$[MNH_4^+]$	[100]	[100]	[100]	[100]	[100]	[100]	[100]
99	$[MH^+]$	100	100	100	100	100	100	39
		[51]	[24]	[16]	[7]	[60]	[86]	[17]
98	$[M^{+\cdot}]$	5	4	4	29	21	3	[56]
		[5]		[2]	[17]	[62]	[1]	
		(0.5)	(0.4)	(0.8)	(2.6)	(2.5)	(0.3)	
97	$[MH^+ - H_2]$				1			32
81	$[MH^+ - H_2O]$	2	12	4	4	3	6	60
71	$[MH^+ - CO]$ or $[MH^+ - C_2H_4]$	3	2	6	15	13	7	100
69	$[MH^+ - CH_2O]$	8	1	1			1	12
		[43]	[1]	[1]		[1]	[3]	[18]
68	$[M^{+\cdot} - CH_2O]$		9				14	
			[13]				[48]	[3]
55	$[MH^+ - CO_2]$	1	1	4	8	2	1	42
				[10]	[36]	[9]		[35]

[a] Regular values are measured by using methane as reagent gas; values in brackets denote ammonia as reagent gas. [b]Values in parentheses obtained by using moist air (33% relative humidity at 25 °C) as reagent gas.

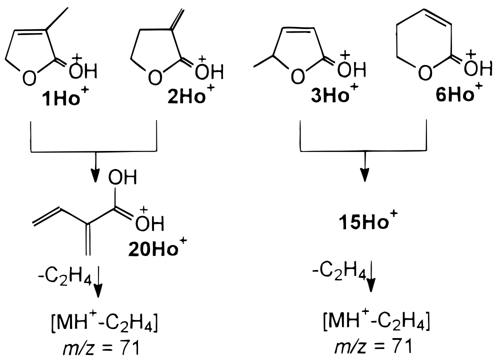
Scheme 5



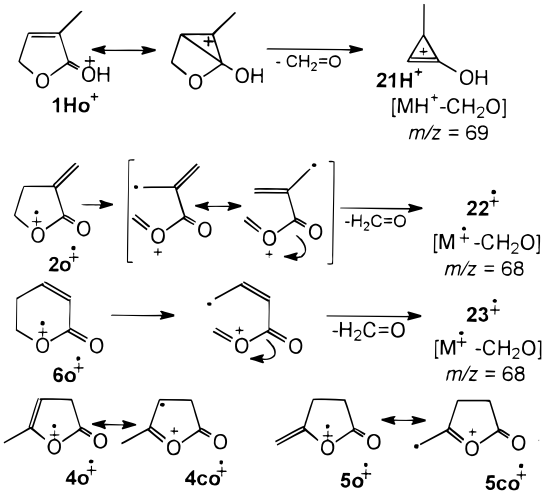
Scheme 6



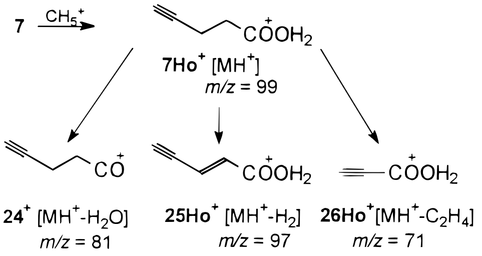
Scheme 7



Scheme 8



Scheme 9



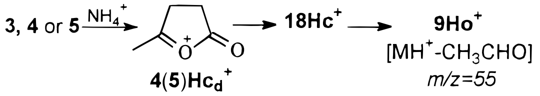
m/z = 69 with strong intensity (see Table 2). This agrees well with the fact that two quite stable species are formed in this fragmentation, i.e., formaldehyde and the aromatic ion **21H**$^+$ (see Scheme 8), and is related to the low internal energy of ions formed with ammonia as a reagent gas. This low energy does not allow fragmentations involving high critical energies.[10] The intensities of the ions $[M^{+\cdot} - CH_2O]$ **22**$^{+\cdot}$ and **23**$^{+\cdot}$ *m/z* = 68 in compounds **2** and **6** are greatly enhanced in the CIMS spectrum with ammonia. Reasons similar to those in the case of compound **1** can be used to explain this observation (see Scheme 8).

The last important fragmentation observed with this reagent gas is the loss of acetaldehyde by γ-substituted lactones **3**−**5** to give the vinylcarbonyl cation $[MH^+ - CH_3CHO]$ (**9Ho**$^+$) *m/z* = 55 (see Experimental Section). This ion can be readily explained by C-protonation in the gas phase to give **4(5)Hc$_d$**$^+$ from which acetaldehyde is lost as ascertained by HRMS (see Scheme 10). This behavior in the gas-phase correlates well with the observed polymerization in solution as reported in Scheme 1.

---

[10] See ref 8, pp 79−80.

Scheme 10



A comparison of the course of the protonation in solution and the mass spectra shows that compounds **1**, **2**, **3**, and **6**, which give rise in solution to stable O-protonated species, give intense [MH$^+$] ions in the CIMS spectrum. Conversely, compounds **4** and **5**, which in solution give the ketoacid $\mathbf{8H_2o^{+2}}$ by ring opening through a C-protonated intermediate, in the gas phase give rise to [MH$^+$] ions as well as [M$^{+\cdot}$] ions generated by charge exchange, which reflects the enhanced stability of the corresponding allylic radical-cations (see Table 2, values in parentheses).

Conclusions

The protonation of α,β-unsaturated lactones takes place on the carbonyl oxygen atom to give rise to the corresponding stable O-protonated species. Conversely, under strong acid conditions, unconjugated lactones yield through the less stable C-protonated species either ring opening by reacting with water present in the reaction medium or decarbonylation in anhydrous conditions. This behavior is consistent with that observed in the gas phase under CIMS conditions. In this case, the different proton affinity of these isomeric lactones results in the formation of different types of ions by mass spectrometry. The very energetic ionization with methane does not allow a precise differentiation between these lactones. A characteristic is the more extensive fragmentation of unconjugated members. However, the ionization with ammonia and moist air reflects the different proton affinities of these compounds. Then, conjugated lactones give O-protonated molecules with noticeable intensity, while charge transfer is the most important process with unconjugated lactones, and the intensity of the molecular ion is greatly enhanced at the expense of the protonated molecules.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded using dioxane as an external standard (capillary tube). Chemical shifts are reported in ppm relative to TMS. Low- and high-resolution CIMS spectra and linked scanning experiments were recorded with a VG Autospec spectrometer with a high-pressure CI source at 150 °C and 70 eV of ionizing electron energy with the repeller at cage potential and a gas cell for metastable studies. The liquid samples were introduced into the mass spectrometer by GC (helium as a carrier gas) using a BPX5 capillary column (25 m, 0.25 mμ, 0.22 mm i.d.). Reagent gas (methane, ammonia, or moist air containing 6.7 g/m^3 water) pressure was estimated to be 0.2 to 0.3 Torr. The ion accelerating potential was 8 kV. Chemical ionizing gases were of the highest purity available. For linked scanning experiments helium was used as collision gas in the first field free region gas cell; the helium was admitted to the collision cell to reduce the main beam intensity to ca. 40%. B^2/E linked scans were used to observe the precursor ions leading to ion $m/z = 71$, when **7** is protonated into the ion source by CH_5^+ by scanning simultaneously the magnet and the electric fields such that B^2/E is maintained constant throughout.

Lactones[11] **1**,[12] **2**, **4**, **5**, and **6** and acid **7** were obtained commercially. Ions were prepared by slowly adding the cooled acid or lactone to a quantity of concentrated sulfuric acid or neat trifluoromethanesulfonic acid sufficient to give a ca. 1 M solution with efficient stirring.

The cationic solutions were heated in tightly closed NMR tubes in a thermostated bath at the temperature indicated in the text.

3-Methyl-2(5*H*)-furanone (1): ^{1}H NMR (CDCl$_3$ 80 MHz): δ 1.9 (m, 3H), 4.8 (m, 2H), 7.2 (m, 1H); ^{13}C NMR (neat, 20 MHz): δ 10.7 (q), 70.0 (t), 129.9 (s), 144.9 (d), 174.8 (s).

3-Methylen-2(4,5*H*)-furanone (2): ^{1}H NMR (CDCl$_3$ 80 MHz): δ 3.0 (m, 2H), 4.4 (t, 2H), 5.7 (d, 1H), 6.2 (d, 1H); ^{13}C NMR (neat, 20 MHz): δ 27.8 (t), 65.8 (t), 122.8 (t), 135.2 (s), 171.4 (s).

5-Methyl-2(5*H*)-furanone (3). This compound was prepared by extending a method described in the literature,[13] by mixing α-bromo-γ-valerolactone with DBU at room temperature in CH$_2$Cl$_2$ solution. ^{1}H NMR (CDCl$_3$, 250 MHz): δ 1.4 (d, 3H), 5.1 (m, 1H), 6.0 (d, 1H), 7.5 (d, 1H); ^{13}C NMR (CDCl$_3$, 62.5 MHz): δ 18.3 (q), 79.4 (d), 120.5 (d), 157.7 (d), 172.9 (s).

2-(5,6*H*)-Pyranone (6): ^{1}H NMR (CDCl$_3$ 80 MHz): δ 2.4 (m, 2H), 3.1 (m, 2H), 3.7 (m, 1H), 4.1 (d, 1H); ^{13}C NMR (neat, 20 MHz): δ 24.3 (t), 67.0 (t), 121.1 (d), 147.7 (d), 164.0 (s).

Additional ^{1}H and ^{13}C NMR Data (δ values) for the Described Ions. 1Ho$^+$: ^{1}H NMR 2.3 (s, 3H), 5.8 (s, 2H), 8.2 (s, 1H); **2Ho$^+$**: ^{1}H NMR 3.2 (t, 2H), 5.1 (t, 2H), 6.5 (s, 1H), 6.9 (s, 1H); **3Ho$^+$**: ^{1}H NMR 1.6 (d, 3H), 6.0 (m, 1H), 6.6 (d, 1H), 8.3 (d, 1H); **4(5)Hc$_d^+$**: ^{1}H NMR 2.6 (s, 3H), 3.1 (t, 2H), 3.3 (t, 2H); ^{13}C NMR 27.8 (t), 28.9 (q), 37.5 (t), 189.6 (s), 234.3 (s); **6Ho$^+$**: ^{1}H NMR 2.9 (dt, 2H), 4.9 (t,2H), 6.4 (d, 1H), 7.8 (dt, 1H); $\mathbf{8H_2o^{+2}}$: ^{1}H NMR 2.9 (s, 4H), 5.8 (s, 1H); ^{13}C NMR 24.1 (t), 116.3 (d), 196.0 (q), 242.3 (q); **11Ho$^+$**: ^{1}H NMR 3.1(s, 4H), 6.1 (s, 1H); ^{13}C NMR 24.2 (t), 67.3 (t), 242.4 (s); **12Ho$^+$**: ^{1}H NMR 5.5 (s, 2H), 6.6 (d, 1H), 8.3 (d, 1H); ^{13}C NMR 84.9 (t), 118.9 (d), 170.7 (d), 189.4 (s).

High-Resolution GC−CI Mass Spectrometry Measurements. Ion set $m/z = 71$: **4H$^+$** Calcd mass for ion [C$_4$H$_7$O]$^+$ [MH$^+$ − CO] 71.0497. Experimental: 71.0500. **5H$^+$** Experimental: 71.0501. **1H$^+$** Calcd mass for ion [C$_3$H$_3$O$_2$]$^+$ [MH$^+$ − C$_2$H$_4$] 71.0133. Experimental: 71.0130. **2H$^+$** Experimental: 71.0130. **6H$^+$** Experimental: 71.0131. Ion set $m/z = 55$: **4H$^+$** Calcd mass for ion [C$_3$H$_3$O]$^+$ [MH$^+$ − CH$_3$CHO] 55.0184. Experimental: 55.0184. **5H$^+$** Experimental: 55.0182.

Acknowledgment. This work was supported by the Spanish Dirección General de Investigación Científica y Técnica (PB96-0757). We gratefully acknowledge the Servicio Central de Soporte a la Investigación Experimental (Universidad de Valencia) for access to their instrumental facilities. We gratefully acknowledge one of our referees for helpful suggestions.

JO991056I

---

[11] Rao, Y. S. *Chem. Rev.* **1976**, *76*, 625.

[12] Crisp, G. T.; Meyer, A. G. *J. Org. Chem.* **1992**, *57*, 6972−6975.

[13] Savoca, A. C. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L..A. Ed.; Vol. 2, pp 1497−1503; John Wiley & Sons: Chichester, 1995. (b) Oediger, H.; Möller, F. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 76.