

## The Structure of the Long-lived Radical Cation of Ethyl Acetate

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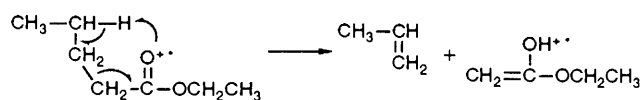
The long-lived radical cation of ethyl acetate exists as its enol form in the gas phase.

The structures of ester radical cations have been the subject of controversy for almost ten years.<sup>1-3</sup> The most recent results based on EPR spectroscopy<sup>1-3</sup> strongly suggest that various simple ester radical cations irreversibly rearrange upon annealing in the solid state at cryogenic temperatures. The reaction is thought<sup>2d</sup> to involve an intramolecular hydrogen atom transfer<sup>4</sup> to the carbonyl oxygen, and to generate a distonic ion with separate charge and radical sites. In sharp contrast to these findings, it has been reported<sup>5,6</sup> on various occasions that gaseous ester radical cations do not lose their original structures in tandem mass spectrometers, although some of these ions apparently partially rearrange prior to dissociation (in the case of ionized methyl acetate, isomerization to a distonic form was suggested).<sup>5</sup> A possible explanation for the different results obtained by using the matrix isolation technique and tandem mass spectrometry lies in the different lifetimes of the ions in these experiments: the matrix isolation experiments involve long-lived ions while tandem mass spectrometry experiments deal with short-lived ions (typically <100  $\mu$ s) that may not have enough time to isomerize. We report here the first gas-phase experimental study on the structures of *low-energy, long-lived* ester radical cations. This study demonstrates that the radical cation of ethyl acetate is kinetically unstable towards isomerization to its *enol form*.

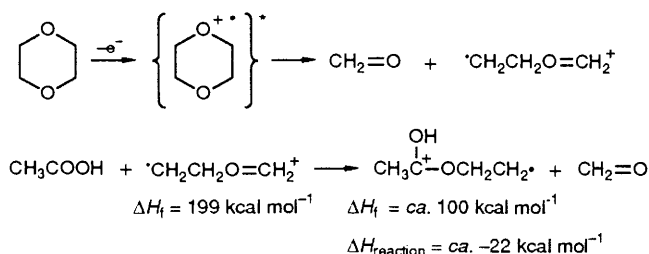
Ethyl acetate was ionized in a dual-cell Fourier transform ion cyclotron resonance mass spectrometer<sup>7</sup> (Extrel FTMS-2001) by electron ionization and by thermoneutral charge exchange with  $\text{CS}_2^{+\cdot}$ , transferred into the other side of the

dual cell, collisionally cooled, and isolated from interfering ions. Different chemical probes were used to examine the structure of the long-lived (>1 s) radical cation. Cyclohexanone has a significantly lower ionization potential (9 eV)<sup>8</sup> than simple organic esters (*e.g.*, ethyl acetate: 10 eV).<sup>8</sup> Therefore, conventional ester radical cations are expected to be rapidly neutralized through charge exchange with cyclohexanone. This was observed to be true, for example, for the radical cations of  $\gamma$ -butyrolactone and  $\delta$ -valerolactone. However, the ethyl acetate radical cation undergoes predominantly proton transfer with cyclohexanone. This finding indicates (*i*) that the ion is a Brønsted acid with a lower heterolytic bond-energy to the proton than protonated cyclohexanone (201.4 kcal mol<sup>-1</sup>),<sup>8</sup> and (*ii*) that the electron affinity of the ion is significantly lower (by more than 20 kcal mol<sup>-1</sup>) than the ionization energy of ethyl acetate (1 cal = 4.184 J). It is concluded that the long-lived ethyl acetate radical cation ( $\Delta H = 125$  kcal mol<sup>-1</sup>)<sup>8</sup> must have isomerized to another structure, most likely either the distonic structure,  $\text{CH}_3\text{C}^+(\text{OH})\text{OCH}_2\text{CH}_2\cdot$  ( $\Delta H = 113$  kcal mol<sup>-1</sup>),<sup>8-10†</sup> by an exothermic 1,5-hydrogen shift,<sup>4</sup> or the enol form,  $\text{CH}_2=\text{C}(\text{OH})\text{OCH}_2\text{CH}_3^{+\cdot}$  ( $\Delta H = 104$  kcal mol<sup>-1</sup>),<sup>8,11</sup> by two consecutive 1,5-hydrogen shifts.

†  $E_d(\text{C-H})$  in the alkoxide methyl group of  $\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{H}^+)$  is estimated to be the same as in protonated ethanol: 106 kcal mol<sup>-1</sup> (ref. 9). The hydrogen atom affinity of  $\text{CH}_3\text{COOCH}_2\text{CH}_3^{+\cdot}$  is 118 kcal mol<sup>-1</sup> (refs. 8, 10).



Scheme 1

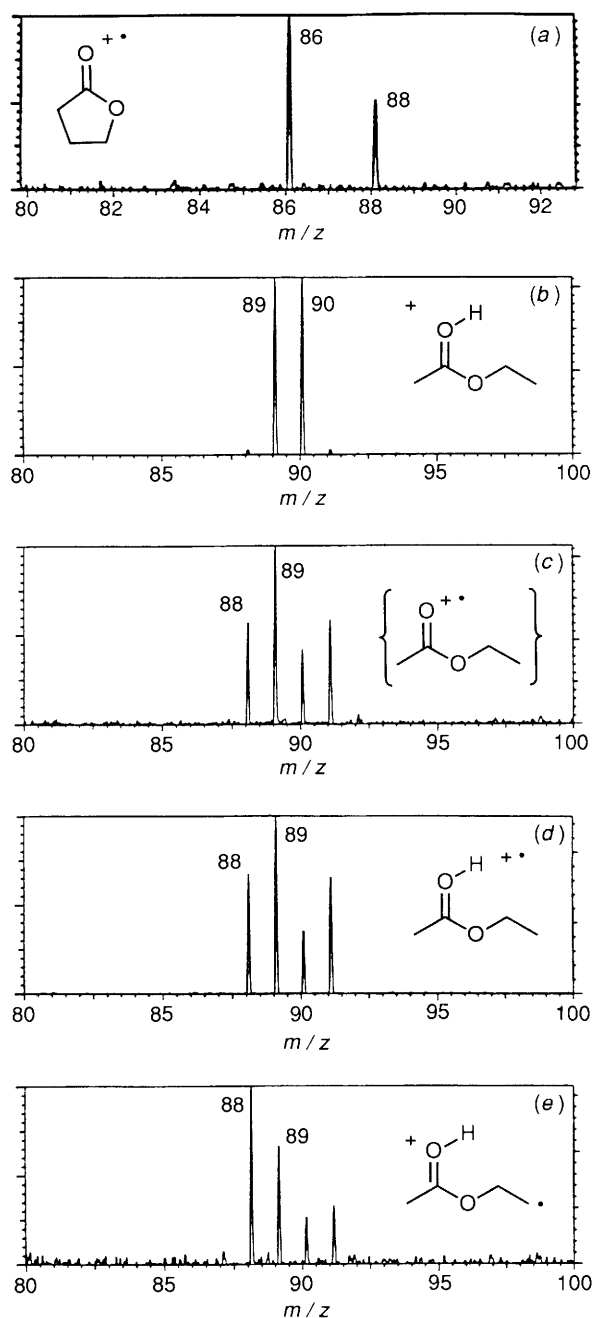


Scheme 2

The enol isomer was generated in the mass spectrometer from ionized ethyl valerate as well as from ionized ethyl butyrate by McLafferty rearrangement (Scheme 1).<sup>11</sup> The distonic isomer,  $\text{CH}_3\text{C}^+(\text{OH})\text{OCH}_2\text{CH}_2^\bullet$ , was synthesized by transferring ionized ethylene to acetic acid from  $\bullet\text{CH}_2\text{CH}_2\text{O}^+ = \text{CH}_2$  (Scheme 2), which in turn was formed<sup>12,13</sup> by electron ionization of 1,4-dioxane pulsed into one side of the dual cell. The distonic and the enol reference ions cannot be distinguished on the basis of their reactions with cyclohexanone since cyclohexanone readily deprotonates both ions. Therefore, decomposition caused by energetic collisions was investigated. Collisional activation<sup>‡</sup> yields a similar product distribution for the ethyl acetate radical cation and the enol reference ion. This distribution, however, is qualitatively different from that of the distonic ion: a fragment ion,  $m/z$  55, is not observed for the distonic ion. While this finding demonstrates that the ethyl acetate radical cation does *not* have the structure of the distonic ion, it does not yield explicit evidence for the similarity of the low-energy structures of the long-lived ester radical cation and its enol form.

Reaction of the enol and the distonic reference ions with  $(\text{CD}_3)_2\text{CDOD}$  or  $\text{CH}_3\text{CO}_2\text{D}$  results in exchange<sup>10,14</sup> of the hydroxy hydrogen with deuterium; the same is observed for related protonated esters [Fig. 1(b)]. At long reaction times, the enol and the distonic ions also produce other ions [Fig. 1(d) and (e)] from processes involving deuterium atom abstraction (hydrogen atom abstraction is observed for these ions with unlabelled propan-2-ol). The distonic reference ion is distinguished from the enol form by a slower reaction rate; protonated ethyl acetate reacts at about the same rate as the distonic ion. *The ethyl acetate radical cation yields a product distribution that is similar in every respect with that obtained for the enol ion, and different from that of the distonic ion* [Fig. 1(c)]. This result unequivocally proves that most of the long-lived ethyl acetate radical cations have the enol structure. In contrast, the radical cations of  $\gamma$ -butyrolactone and  $\delta$ -valerolactone do not readily isomerize in the gas phase, as indicated by dominant deuterium atom abstraction for both of these ions [see Fig. 1(a)]. It is concluded that the isomerization of the ethyl acetate radical cation does not occur *via* a process involving a series of intermolecular hydrogen atom or proton transfers since this should occur equally readily for the cyclic and the acyclic esters.

Rearrangement of the ethyl acetate radical cation to the enol form which is likely to represent the global minimum on the potential energy surface<sup>5d,e</sup> is expected to take place *via* the distonic structure.<sup>5</sup> The findings presented in this paper



**Fig. 1** (a) Reaction of  $[\text{2H}_8]$ propan-2-ol with the radical cation of  $\gamma$ -butyrolactone ( $m/z$  86) results in deuterium atom abstraction (reaction time 100 ms), while the reaction of  $[\text{2H}_8]$ isopropan-2-ol with (b) protonated ethyl acetate ( $m/z$  89), (c) the radical cation of ethyl acetate ( $m/z$  88), (d) the enol reference ion ( $m/z$  88), and (e) the distonic reference ion results in predominant hydrogen–deuterium exchange (reaction time 2 s). All the reactions were measured at a nominal pressure of  $[\text{2H}_8]$ isopropan-2-ol of  $1.2 \times 10^{-7}$  Torr.

therefore indicate that *the energy barriers for isomerization of the conventional radical cation to the distonic form, and of the distonic form to the enol ion, must be near or below the heat of formation for the conventional radical cation, and that this radical cation is kinetically unstable*. A full manuscript showing similar results for other long-lived ester radical cations is in preparation.

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‡ Argon target, 100 ms reaction time, laboratory collision energies 20–150 eV were used.

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