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JMS Letters

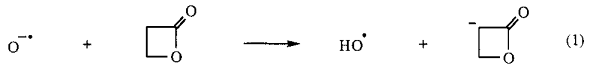
Dear Sir,

Formation of the Distonic Acetate Radical Anion $^{\bullet}CH_2CO_2^-$ in Reactions of $O^{-\bullet}$ with Lactones in the Gas Phase

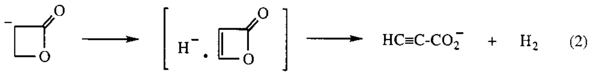
The reactivity and stability of radical anions in the gas phase have been a subject of increasing interest in recent years.[1,2] Most of the reported studies of radical anions in the gas phase were focused on the determination of thermodynamic properties, such as electron affinities of the related neutral molecules and the acidities of radicals.[2–4] Much less is known about the reactivity of radical anions in gas-phase ion–molecule reactions, irrespective of the fact that these ions may react either as a nucleophile or as a radical. In this respect, distonic radical anions are of special interest since the radical and charge centers are located in a formal sense on distinct atoms.[5,6] However, only a few examples of this class of ions have been characterized, owing mainly to the fact that these species are not readily generated in the gas phase. One possible route to the formation of distonic radical anions in the gas phase is provided by the formal $H_2^{+\bullet}$ abstraction, which occurs in the reactions of the $O^{-\bullet}$ ion with a variety of organic molecules.[7,8] For example, $O^{-\bullet}$ is reported to react with CH_3SCH_2CN by a 1,3-$H_2^{+\bullet}$ abstraction with the formation of a distonic $^{\bullet}CH_2S$—$\bar{C}HCN$ ion[9] and, likewise, in the reaction with acetone a $^{\bullet}CH_2$—C(O)—CH_2^- ion arises.[10] Other studies reveal that distonic $^{\bullet}C_6H_4CO_2^-$ radical anions are formed by the addition of CO_2 to the 1,2-dehydrobenzene radical anion,[11] whereas the distonic acetate ion $^{\bullet}CH_2CO_2^-$ is indicated to be generated in the reaction of CH_3—$\bar{C}$=O with O_2,[12] and also upon high kinetic energy collision-induced dissociation of monocarboxylate anions generated from diethyl glutarate and dimethyl 3,3-dimethylglutarate.[13] More recently, a number of distonic radical anions, including the $^{\bullet}CH_2CO_2^-$ ion, were generated by reacting various carbanions containing a trimethylsilyl group with F_2 at a relatively high pressure (~70 Pa of He bath gas) in a flowing afterglow instrument.[14,15] In this letter, we report on the reactions of the radical anions $O^{-\bullet}$ and $CHF^{-\bullet}$ with the selected carbonyl containing cyclic compounds, β-propiolactone and β-butyrolactone. These reactant systems were chosen in order to examine the possibility of the formation of distonic radical anions in ion–molecule reactions occurring between readily accessible reactant ions and convenient substrates for the low-pressure conditions typical of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer designed and constructed at the University of Amsterdam.[16]

Reactions with β-propiolactone

The $O^{-\bullet}$ ions were generated by capture of 1.2 eV electrons by N_2O in a dissociative process which yields ions with an average kinetic energy of 0.4 eV.[7,8] The $O^{-\bullet}$ ions react with β-propiolactone in part by proton abstraction with formation of $[M - H]^-$ ions as indicated in Eqn (1) and Table 1.

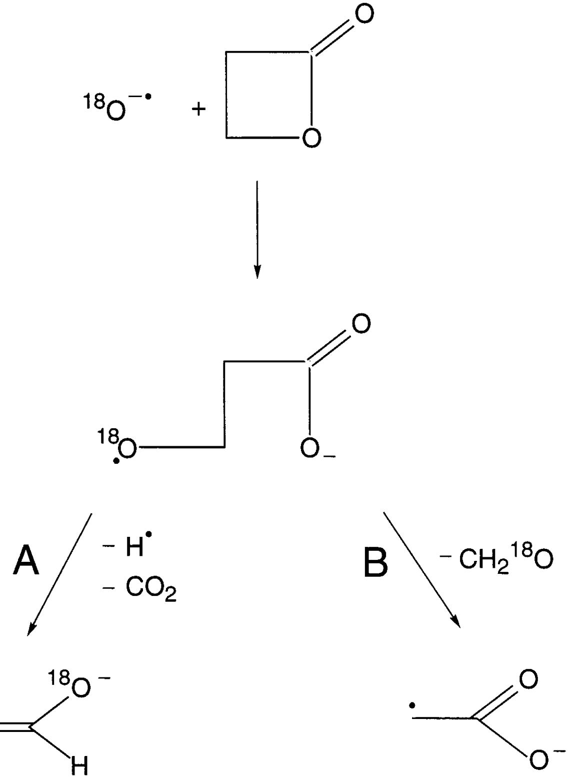


The $[M - H]^-$ ions may react further to form an ion–neutral complex composed of a hydride ion and an unsaturated lactone as shown in Eqn (2).[17] Subsequently, the complex can react by proton transfer accompanied by ring opening and the loss of H_2 to yield HC≡C—CO_2^- ions. In the reaction of the $^{18}O^{-\bullet}$ ion with the lactone (Table 1), the label is not incorporated into the =$[M - H]^-$ and HC≡C—CO_2^- ions, in agreement with these mechanistic considerations.



The $O^{-\bullet}$ ion also reacts with β-propiolactone by a formal abstraction of $H_2^{+\bullet}$, thus forming $[M - H_2]^{-\bullet}$ radical anions in a low relative yield (Table 1). The properties of the $[M - H_2]^{-\bullet}$ radial anions were not examined in the present study owing in part to the observation that these ions react readily with the neutral species in the FT-ICR cell. In addition to the $[M - H_2]^{-\bullet}$ ions, minor amounts of CH_2=CHO^- ions are formed in a process that results in the incorporation of the reactant ion as revealed by the observation that CH_2=$CH^{18}O^-$ ions are generated in the experiments with the $^{18}O^{-\bullet}$ ions. A possible route to the enolate anions could involve initial attack on the β-carbon atom followed by loss of an $H^{\bullet}$ atom and CO_2 as visualized in Scheme 1 (pathway A). Overall, the reaction enthalpy of this process is estimated to be -165 kJ mol^{-1}.[18]

The key observation for the $O^{-\bullet}$/β-propiolactone system is that ions are formed which can be assigned a $^{\bullet}CH_2CO_2^-$ structure (see below). These distonic acetate radical anions are formed in a normalized yield of 10% in a process which may involve attack on the carbon atom of the β-methylene group followed by the loss of a formaldehyde molecule (Scheme 1, pathway B). Overall, this process is estimated to be exothermic by 270 kJ mol^{-1} (Table 1).[18] The occurrence of such a pathway is supported by the finding that only unlabeled acetate radical anions are formed in the reaction of $^{18}O^{-\bullet}$ with β-propiolactone.



Scheme 1. Proposed mechanism for the formation of the CH_2=$CH^{18}O^-$ and $^{\bullet}CH_2CO_2^-$ ions in the reaction of $^{18}O^{-\bullet}$ with β-propiolactone.

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Table 1. Normalized abundances of product ions formed in the reaction of the atomic oxygen radical anion and the $CHF^{-\cdot}$ ion with the substrates, β-propiolactone and β-butyrolactone, together with the estimated reaction enthalpies (see also text)[a]

Reactant ion	Substrate	Product ion	Normalized abundance(%)	$\Delta_r H^\circ$ (kJ mol^{-1})[b]
$O^{-\cdot}$	β-Propiolactone	$CH_2{=}CHO^-$	10	−165
		$^{\cdot}CH_2CO_2{}^-$	10	−270
		$HC{\equiv}CCO_2{}^-$	35	
		$[M-H_2]^{-\cdot}$	10	
		$[M-H]$	35	
$^{18}O^{-\cdot}$ [c]	β-Propiolactone	$CH_2{=}CH\,^{18}O^-$	5	
		$^{\cdot}CH_2CO_2{}^-$	10	
		$HC{\equiv}CCO_2{}^-$	35	
		$[M-H_2]^{-\cdot}$	5	
		$[M-H]^-$	45	
$CHF^{-\cdot}$ [d]	β-Propiolactone	$^{\cdot}CH_2CO_2{}^-$	5	−285
		$[M-H]^-$	90	
		$C_4H_3O_2{}^-$	5	
$O^{-\cdot}$	β-Butyrolactone	$^{\cdot}CH_2CO_2{}^-$	5	−275
		$HC{\equiv}CCO_2{}^-$	10	
		$CH_3C{\equiv}CCO_2{}^-$	35	
		$[M-H]^-$	50	
$^{18}O^{-\cdot}$ [c]	β-Butyrolactone	$^{\cdot}CH_2CO_2{}^-$	5	
		$HC{\equiv}CCO_2{}^-$	10	
		$CH_3C{\equiv}CCO_2{}^-$	30	
		$[M-H]^-$	55	

[a] Relative yields of product ions after a reaction time of 150–200 ms. At these reaction times the conversion into products was typically 60–70%. The relative yields are reproducible to within 5%.

[b] The reaction enthalpies were estimated on the basis of data given in Ref. 18. The average uncertainty on the values given is 12–20 kJ mol^{-1}.

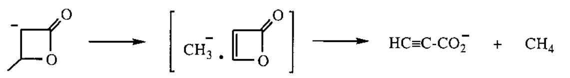
[c] The $^{18}O^{-\cdot}$ ions were formed by reacting $O^{-\cdot}$ with $H_2{}^{18}O$ (see Ref. 8).

[d] The $CHF^{-\cdot}$ ions were generated by allowing $O^{-\cdot}$ to react with CH_3F (see Refs 2 and 8).

The $CHF^{-\cdot}$ ion reacts similarly to the $O^{-\cdot}$ ion with β-propiolactone, that is, ions with an assigned structure of $^{\cdot}CH_2CO_2{}^-$ are formed in a normalized yield of 5% together with $[M-H]^-$ ions and species with an assigned elemental composition of $C_4H_3O_2$ (Table 1). Part of the $[M-H]^-$ ions could be expected to expel H_2 as observed in the experiments with the $O^{-\cdot}$ ion. Possibly the absence of product ions of such a reaction pathway may indicate that the $[M-H]^-$ ions are formed in the reaction with $CHF^{-\cdot}$ with insufficient internal energy to react further. By contrast, in the reaction between the non-thermalized $O^{-\cdot}$ ions (see above) and β-propiolactone, proton abstraction may lead to $[M-H]^-$ ions with sufficient internal energy to undergo the reaction sequence shown in Eqn (2).

Reactions with β-butyrolactone

The $O^{-\cdot}$ ion reacts similarly with β-butyrolactone as with β-propiolactone (Table 1) in the sense that the main product ions can be ascribed to proton abstraction which may be followed by the loss of H_2 by a route comparable to that shown for the $O^{-\cdot}$/β-propiolactone system in Eqn (2). In addition, the $O^{-\cdot}$ ion reacts with β-butyrolactone to yield minor amounts of ions with an assigned structure $HC{\equiv}CCO_2{}^-$. These latter ions may be proposed to arise by initial proton abstraction followed by the formation of an ion–neutral complex containing a $CH_3{}^-$ ion and the lactone shown in Eqn (3).[17] Proton abstraction and ring opening may then occur and lead to the formation of the $HC{\equiv}CCO_2{}^-$ ions. In agreement with this suggestion, the label is not incorporated in the $HC{\equiv}CCO_2{}^-$ ions if $^{18}O^{-\cdot}$ is the reactant species.



(3)

Significantly, both the $O^{-\cdot}$ and $^{18}O^{-\cdot}$ ions react with β-butyrolactone to yield the $^{\cdot}CH_2CO_2{}^-$ radical anions. The formation of $^{\cdot}CH_2CO_2{}^-$ ions also in these systems substantiates the mechanistic proposal shown in Scheme 1.

Preliminary attempts to generate ions with a $^{\cdot}CH_2CH_2CO_2{}^-$ structure by reacting the $CHF^{-\cdot}$ or $O^{-\cdot}$ radical anion with γ-butyrolactone failed. The main reaction pathway with this substrate appeared to be proton abstraction for the carbene radical anion and in the reaction with $O^{-\cdot}$, proton transfer competes with formation of $C_3H_2O^{-\cdot}$ radical anions.

Structure and reactivity of the $^{\cdot}CH_2CO_2{}^-$ ions

In order to ascertain the assigned structure of the $^{\cdot}CH_2CO_2{}^-$ ions, these were allowed to react with a series of selected substrates. In agreement with a flowing afterglow study of the $^{\cdot}CH_2CO_2{}^-$ ion,[15] we observe a facile reaction with SO_2 with the formation of $^{\cdot}CH_2SO_2{}^-$ ions and a slow reaction with CH_3SSCH_3 involving abstraction of a CH_3S group and the formation of a $CH_3SCH_2CO_2{}^-$ ion. The occurrence of these reactions provides evidence for the generation of distonic acetate radical anions in the reaction of the $O^{-\bullet}$ ion with the present lactones.

No reaction occurs between $^{\bullet}CH_2CO_2{}^-$ and $^{13}CO_2$, indicating that thermoneutral exchange of the CO_2 unit is too slow to be observed with the present experimental method. The $^{\bullet}CH_2CO_2{}^-$ ion also appears unreactive towards CS_2 and allyl methyl thioether. The absence of reaction with the allyl methyl thioether [Eqn (4)] is intriguing because hydrogen atom abstraction would be expected to be exothermic. This supposition is based on the reported bond dissociation enthalpy (BDE) of 392 ± 17 kJ mol^{-1} for the C—H bond in the $CH_3CO_2{}^-$ acetate anion[15] in combination with the fact that the C—H BDE of the methylene group in the allyl methyl thioether is likely to be slightly lower than that of the methyl group in propene (362 ± 6 kJ mol^{-1}),[18] in keeping with the expected stabilization of the radical center by the sulfur atom in the radical shown in Eqn (4).

$$^{\bullet}CH_2CO_2{}^- + CH_2{=}CH{-}CH_2{-}S{-}CH_3 \not\longrightarrow CH_3CO_2{}^- + CH_2{=}CH{-}{}^{\bullet}CH{-}S{-}CH_3 \qquad (4)$$

A formal atom abstraction process is observed in the reactions of the $^{\bullet}CH_2CO_2{}^-$ ion with some halogen-substituted methanes. In particular, bromine atom abstraction occurs in the reactions with CBr_4 and $CFBr_3$. With CBr_4 as the substrate, bromine atom abstraction with formation of a $BrCH_2CO_2{}^-$ ion [Eqn (5)] is estimated to be exothermic by about 45 kJ mol^{-1}.[15,18]

$$^{\bullet}CH_2CO_2{}^- + CBr_4 \rightarrow BrCH_2CO_2{}^- + CBr_3{}^{\bullet} \qquad (5)$$

With CH_2ClI, iodine atom abstraction is observed and estimated to be exothermic by 61 kJ mol^{-1} provided $ICH_2CO_2{}^-$ ions are generated.[15,18] Abstraction of a chlorine atom does not occur in the reaction with CH_2ClI even though this process is indicated to be slightly exothermic, that is, $\Delta H_r^\circ = -10$ kJ mol^{-1}. In addition, no reaction is observed between $^{\bullet}CH_2CO_2{}^-$ and CH_3I, in spite of the fact that formation of $ICH_2CO_2{}^-$ ions by iodine atom abstraction is estimated to be exothermic by ~ 50 kJ mol^{-1}. These thermodynamic considerations imply that the halogen atom abstraction from a halomethane by the distonic acetate radical anion can be hindered by a kinetic energy barrier.

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Yours,

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