O^{-•} Chemical Ionization of Carbonyl Compounds

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The negative ion chemical ionization mass spectra of twentyeight C₄ to C₇ carbonyl compounds were recorded using the oxide radical anion O^{-•} as reagent ion. As noted earlier, the reactions occurring include H⁺ abstraction, H₂⁺ abstraction, H-atom displacement, and alkyl radical displacement. In addition, the [M-2H]⁻ ions fragment further by alkyl radical elimination. The relative importance of these reactions depends strongly on molecular structure, with the result that isomer distinction frequently is possible. Where this is not possible, as for isomeric aldehydes, the collisional charge inversion mass spectra of common product ions provides isomer distinction. The H₂⁺ abstraction reaction is shown to involve abstraction not only of two hydrogens from the same α-carbon but also, in part, abstraction of one hydrogen from each α-carbon. (*J Am Soc Mass Spectrom* 1991, 2, 292-298)

The oxide radical anion O^{-•} is unusual among negative ion chemical ionization (CI) reagent ions in that not only is it a strong Brønsted base but also it is a radical. Thus, it reacts with organic substrates not only by proton abstraction, typical of Brønsted bases, but also by H atom abstraction, by H₂⁺ abstraction, and by H atom and alkyl radical displacement [1-7]. This variety of reaction pathways creates the possibility that O^{-•} CI can provide more structure information than other negative ion reagents and this has been amply demonstrated in a number of preliminary studies [3-6].

Earlier studies [3, 5] reported a survey of the reactions of O^{-•} with a limited number of carbonyl compounds. The reaction pathways with ketones that were elucidated were as follows.

The OH⁻ produced in reaction 1 may react further with the ketone to produce [M-H]⁻ [3]. Based on the limited number of compounds studied the spectra reported showed considerable potential in distinguishing among isomeric carbonyl compounds.

The present work reports a detailed study of the O^{-•} CI mass spectra of the available C₄ to C₇ carbonyl compounds to explore more fully the utility of O^{-•} CI to distinguish among isomeric carbonyl compounds. Where isomer distinction from the CI mass spectra is not possible, the usefulness of collision-induced charge inversion mass spectra [8] of selected ions in distinguishing among isomers is explored. Very recently, Sürig and Grutzmacher [9] showed the analytical utility of such experiments in a study of the enolate ions of some open-chain and cyclic ketones.

Experimental

All experimental work was carried out using a VG Analytical ZAB-2FQ (VG Analytical Ltd., Wythenshawe, Manchester, UK) hybrid BEQQ mass spectrometer [10]. Briefly, the instrument is a reversed geometry (BE) double-focusing mass spectrometer with a third stage consisting of a deceleration lens system, a radiofrequency-only quadrupole collision cell, and a quadrupole mass analyzer.

The O^{-•} reactant ion was produced by electron impact on a 90% N₂ - 10% N₂O mixture with the combined electron ionization/chemical ionization source operating in the CI mode. The reagent gas

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pressure was approximately 10^{-4} torr as read on the ionization gauge attached to the source housing. Spectra were recorded with the instrument operating in the double-focusing mode with a source temperature of 250 °C and an accelerating voltage of 8 kV. Samples were introduced through a heated inlet line.

Metastable ion mass spectra were recorded by mass selecting the ion of interest and monitoring the fragmentation products produced in the field-free region between the magnetic and electric sectors by scanning the electric sector. Charge inversion mass spectra were obtained by mass selecting the ions of interest with the magnetic sector, following which they underwent collision with O₂ collision gas in the collision cell (CC 2) located at the focal point between the magnetic and electric sectors. The positively charged product ions were analyzed according to their kinetic energy by scanning the electric sector voltage, the polarity having been set to transmit the positive ions. The kinetic energy of the mass-selected ions was 8 keV and the collision gas pressure was adjusted to give approximately 30% reduction of the mass-selected ion beam. Low energy collision-induced dissociation mass spectra were recorded as a function of collision energy by mass selecting the appropriate ion beam at 6 keV ion energy by the double-focusing BE instrument, decelerating the beam to the appropriate energy (10 to 40 eV, laboratory scale), and introducing the ion beam into the radiofrequency-only collision cell with N₂ collision gas at an indicated pressure of 2×10^{-7} torr. The product fragment ions were analyzed with the final quadrupole mass analyzer.

The relative intensities in both the mass spectra and the collisional mass spectra were reproducible to within $\pm 5\%$. The carbonyl compounds were commercial samples of high purity that were used as received. 2-Pentanone-1, 1, 1, 3, 3-d₅ was obtained from MSD Isotopes, Montreal, Canada.

Results and Discussion

C₄ Carbonyl Compounds

The O^{-•} CI mass spectra of butanone, butanal, and isobutanal are recorded in Table 1. The spectrum obtained for butanone illustrates the full range of

Figure 1. Charge-inversion mass spectra of $n\text{-C}_3\text{H}_7\text{CO}_2^-$ and $i\text{-C}_3\text{H}_7\text{CO}_2^-$ derived from the butanals by H-atom displacement.

reaction pathways outlined in reactions 2 to 6. By the same token, the mass spectra recorded for the two aldehydes illustrate the reaction pathways of O^{-•} with aldehydes, viz,

The mass spectra for the two aldehydes do not permit a clear distinction between the two isomers. However, distinction is possible from the charge inversion mass spectra of the C₃H₇CO₂⁻ carboxylate product ions. As shown in Figure 1, the m/z 43 (C₃H₇⁺) ion signal is much more prominent in the spectrum of the carboxylate ion derived from isobutanal, whereas m/z 60 (C₂H₄O₂⁺) is much more prominent in the spectrum of the carboxylate ion derived from butanal.

C₅ Carbonyl Compounds

The O^{-•} CI mass spectra of 2-pentanone, 3-methyl-2-butanone, 3-pentanone, pentanal, 2-methylbutanal, 3-methylbutanal, and trimethylacetaldehyde are recorded in Table 2. Clearly, the three ketones can be distinguished from each other and from the aldehydes with no difficulty. However, the four aldehydes give similar mass spectra. Some distinction is possible from the charge inversion mass spectra of the C₄H₉CO₂⁻ carboxylate product ions. As shown in

Table 1. O^{-•} Chemical ionization mass spectra of C₄ carbonyl compounds

m/z	Ion	Percent of base peak		
		Butanone	Butanal	Isobutanal
87	C ₃ H ₇ CO ₂ ⁻		70	91
73	C ₂ H ₅ CO ₂ ⁻	9		
71	[M-H] ⁻	100	100	100
70	[M-2H] ⁻	42		
59	CH ₃ CO ₂ ⁻	9		
55	CH ₃ CCO ⁻	7		
45	HCO ₂ ⁻		19	29
41	HCCO ⁻	23		

Table 2. $O^{\cdot-}$ Chemical ionization mass spectra of C_5 carbonyl compounds

m/z	Ion	Percent of base peak					
		2-Pent-anone	3-Methyl-2-butanone	3-Pent-anone	Pent-anal	2-Methyl-butanal	3-Methyl-butanal
101	$C_4H_9CO_2^-$				94	100	100
87	$C_3H_7CO_2^-$	17	20				
85	$[M-H]^-$	100	100	100	100	42	73
84	$[M-2H]^-$	88	13	31			
73	$C_2H_5CO_2^-$			42			
69	$[M-2H-CH_3]^-$	52					
59	$CH_3CO_2^-$	18	17				
55	CH_3CCO^-			10			
45	HCO_2^-				38	40	34
41	$HCCO^-$	61	75				

*Me₃ acetald = trimethylacetaldehyde.

Figure 2, the $C_4H_9^+$ (m/z 57) ion dominates the charge inversion mass spectrum of the carboxylate ion derived from trimethylacetaldehyde but decreases in intensity, relative to the fragment ions $C_3H_7^+$ (m/z 41), $C_3H_3^+$ (m/z 39), $C_2H_5^+$ (m/z 29), and $C_2H_3^+$ (m/z 27), as the butyl group in the carboxylate ion changes from *s*-butyl to isobutyl to *n*-butyl. These intensities parallel the stabilities of the butyl cations. Clearly,

Figure 2. Charge-inversion mass spectra of $C_4H_9CO_2^-$ ions derived from the isomeric C_5 aldehydes by H-atom displacement.

with reference spectra available the aldehyde could be identified from the charge inversion mass spectra of the $[M-H+O]^-$ ions.

The $O^{\cdot-}$ CI mass spectrum of 2-pentanone-1, 1, 1, 3, 3-d₅ also was determined and is compared in Figure 3 with the spectrum obtained for the unlabeled pentanone. The mass shifts for the labeled ketone are as expected, except that a portion of the m/z 69 fragment ion intensity shifts to m/z 72. Metastable ion studies showed that the m/z 72 fragment originated by loss of CH_3 from the $[M-2D]^-$ ion. The m/z 69 fragment ion clearly originates by the reaction sequence.

Although earlier work [3, 5] suggested that H_2^+/D_2^+ abstraction occurred from the same α -carbon, the observation of m/z 72 can be most readily rationalized by the reaction sequence

Figure 3. $O^{\cdot-}$ chemical ionization mass spectra of 2-pentanone and 2-pentanone-1,1,1,3,3-d₅.

Table 3. O^{-•} Chemical ionization mass spectra of C₆ ketones

<i>m/z</i> Ion	Percent of base peak					
	2-Hex-anone	3-Methyl-2-pentanone	4-Methyl-2-pentanone	3,3-Methyl-2-butanone	3-Hex-anone	2-Methyl-3-pentanone
101 C ₆ H ₉ CO ₂ ⁻	15	15	11	14		
99 [M-H] ⁻	100	100	100	100	100	100
98 [M-2H] ^{-•}	59		65			
87 C ₃ H ₇ CO ₂ ⁻					23	37
83 [M-2H-CH ₃] ⁻	24		55			
73 C ₂ H ₅ CO ₂ ⁻					22	31
69 [M-2H-C ₂ H ₅] ⁻	18					
59 CH ₃ CO ₂ ⁻	35	15	9	12		
41 HCCO ⁻	16	38	11	48

forming the deuterium-labeled enolate ion of methyl vinyl ketone. Further evidence for this reaction sequence will be presented below with reference to the spectrum obtained for 2-hexanone. It should be noted that Dawson et al. [11] reported some years ago that O^{-•} reacted with acetone in part by 1, 3-H₂⁺ abstraction.

C₆ Carbonyl Compounds

The O^{-•} CI mass spectra of six C₆ ketones are presented in Table 3, whereas the spectra of three C₆ aldehydes are presented in Table 4. In general, the spectra of Table 3 can be accommodated within the framework of reactions 2 to 6, with the exception of the formation of the *m/z* 69, [M-2H-C₂H₅]⁻ ion in the spectrum obtained for 2-hexanone. That this ion is formed by fragmentation of the [M-2H]^{-•} ion was shown by metastable ion studies. The mechanism of formation presumably is analogous to reaction 10, viz

To provide evidence that the product ion is, in fact, the enolate ion of methyl vinyl ketone, the charge

inversion mass spectrum of the *m/z* 69 ion from 2-hexanone was compared with the charge inversion mass spectrum of the [M-H]⁻ ion derived by reaction of OH⁻ with methyl vinyl ketone. The excellent agreement of the two spectra (Figure 4) provides strong support for the reaction sequence 12. Further supporting evidence (Figure 5) comes from a study of the low energy collision-induced dissociation of the two ions as a function of collision energy. The excellent agreement of the two breakdown graphs leaves little doubt that the two ions have the same structure.

No [M-2H]^{-•} ions are observed in the CI mass spectra of 3-methyl-2-pentanone or 3, 3-dimethyl-2-butanone, although in both cases HCCO⁻ ions are observed, characteristic of fragmentation of the [M-2H]^{-•} ions derived by H₂⁺ abstraction from carbon 1. It appears that complete fragmentation of the

Figure 4. Charge-inversion mass spectra of *m/z* 69 ions from 2-hexanone and from methyl vinyl ketone.**Table 4.** O^{-•} Chemical ionization mass spectra of C₆ aldehydes

<i>m/z</i> Ion	Percent of base peak		
	Hexanal	2-Methyl-pentanal	2-Ethyl-butanal
115 C ₅ H ₁₁ CO ₂ ⁻	90	100	100
99 [M-H] ⁻	100	74	80
45 HCO ₂ ⁻	40	45	33

Figure 5. Breakdown graphs for m/z 69 ions from 2-hexanone and from methyl vinyl ketone.

$[M-2H]^{-}$ ion has occurred. More surprising is the failure to observe either $[M-2H]^{-}$ ions or their fragmentation products in the spectra of 3-hexanone and 2-methyl-3-pentanone. There is no obvious reason why H_2^{+} -abstraction from these ketones does not occur. The O^{-} CI mass spectra of these two ketones are very similar. However, as shown in Figure 6, they can be distinguished on the basis of the charge inversion mass spectra of the $[M-H]^{-}$ ions. As the spectra show there are major differences in the relative intensities of the m/z 43, 55, 56, and 57 ion signals for the two $[M-H]^{-}$ ions. As shown in Table 3, the CI mass spectra of 3-methyl-2-pentanone and 3,3-dimethylbutanone are also very similar although different from the other ketones. Again the charge inversion mass spectra of the $[M-H]^{-}$ ions (Figure 7) show substantial differences, particularly in the intensity of the m/z 57 ion signal relative to other ion signals in the spectra, which allow distinction between the two isomers.

The O^{-} CI mass spectra of the three C_6 aldehydes examined are very similar, Table 4, showing $[M-H]^{-}$, $HCCO_2^{-}$, and $C_5H_{11}CO_2^{-}$ ion signals with similar intensities. However, once again, there are substantial differences in the charge-inversion mass spectra of the $C_5H_{11}CO_2^{-}$ product ions (Figure 8) that permit identification of each isomer. This is achieved primarily by the intensities of the m/z 55 ion signal relative to the m/z 43, 41, and 39 ion signals. It is well known [12, 13] that $C_5H_{11}^{+}$ cations fragment by loss of CH_4 to form $C_4H_7^{+}$ (m/z 55) and by loss of C_2H_4 to form $C_3H_7^{+}$ (which fragments further to $C_3H_5^{+}$ and $C_3H_3^{+}$). The present results indicate that the positive ion formed by charge inversion loses CO_2 to form pentyl ions which show different branching ratios for these two major fragmentation reaction channels.

Figure 6. Charge-inversion mass spectra of $[M-H]^{-}$ ions from 3-hexanone and from 2-methyl-3-pentanone.

C_7 Carbonyl Compounds

The O^{-} CI mass spectra of ten C_7 ketones are recorded in Tables 5 and 6. The ketones with the carbonyl function in the 2-position (Table 5) are clearly identified by the $C_5H_{11}CO_2^{-}$ and $CH_3CO_2^{-}$ carboxyl-

Figure 7. Charge-inversion mass spectra of $[M-H]^{-}$ ions from 3-methyl-2-pentanone and 3,3-dimethyl-2-butanone.

Figure 8. Charge-inversion mass spectra of $C_5H_{11}CO_2^-$ ions derived from the isomeric C_6 aldehydes by H-atom displacement.

ate anions formed. The individual isomers are distinguished from each other primarily by the different fragment ions arising from further decomposition of the $[M-2H]^-$ ions. Of particular note are the $[M-2H-C_3H_7]^-$ ion observed in the spectra of 2-heptanone and 5-methyl-2-hexanone and the $[M-2H-C_2H_5]^-$ ion observed in the mass spectrum of 4-methyl-2-hexanone; these ions must arise by fragmentation of the $[M-2H]^-$ ion arising by 1, 3- H_2^+ abstraction. Of particular interest is the observation that the three di-propyl ketones of Table 6, di-*n*-propyl ketone (4-heptanone), *n*-propyl *i*-propyl ketone (2-methyl-3-hexanone), and di-*i*-propyl ketone (2, 4-dimethyl-3-pentanone), can be distinguished from each other on the basis of their O^{-•} CI mass spectra. Note that di-*i*-propyl ketone shows no $[M-2H]^-$ ion signal nor fragments derived therefrom. Apparently H_2^+ -abstraction does not occur when both enolic hydrogens are tertiary.

Conclusions

The present work extends considerably earlier studies [3, 5] of the reactions of O^{-•} with carbonyl compounds and shows that O^{-•} CI is capable of positively identifying many carbonyl compounds. Where such identification is not possible from the CI mass spectra alone, the present study has shown that the charge-inversion mass spectra of selected common ions often provides isomer distinction.

Table 5. O^{-•} Chemical ionization mass spectra of C_7 methyl ketones

m/z ion		Percent of base peak				
		2-Heptanone	3-Methyl-2-hexanone	4-Methyl-2-hexanone	5-Methyl-2-hexanone	4,4-Me ₂ -2-pentanone
115	$C_7H_{13}CO_2^-$	15	16	13	14	12
113	$[M-H]^-$	100	100	100	100	100
111	$[M-2H]^-$	43	7	59	39	95
97	$[M-2H-CH_3]^-$			25	16	68
83	$[M-2H-C_2H_5]^-$			20		
69	$[M-2H-C_3H_7]^-$	16			30	
59	$CH_3CO_2^-$	15	19	9	16	9
41	$HCCO^-$	22	29	13	24	18

*4,4-Me₂-2-pentanone = 4,4-dimethyl-2-pentanone.

Table 6. O^{-•} Chemical ionization mass spectra of C_7 ketones

m/z ion		Percent of base peak				
		3-Heptanone	2,4-Me ₂ -3-pentanone	2-Methyl-3-hexanone	4-Heptanone	2,2-Me ₂ -3-pentanone
113	$[M-H]^-$	100	97	100	100	100
112	$[M-2H]^-$	46		12	51	
101	$C_4H_9CO_2^-$					26
97	$[M-2H-CH_3]^-$				18	
87	$C_3H_7CO_2^-$		100	47	38	
83	$[M-2H-C_2H_5]^-$	29				
73	$C_2H_5CO_2^-$	14				24
69	$[M-2H-C_3H_7]^-$			9	8	

*2,4-Me₂-3-pentanone = 2,4-dimethyl-3-pentanone.

**2,2-Me₂-3-pentanone = 2,2-dimethyl-3-pentanone.

The present results concerning the charge inversion of carboxylate ions (Figures 1, 2, and 8) are in agreement with earlier studies [8] which have shown that loss of CO_2 from the initial RCO_2^+ ion is a major fragmentation pathway. Mechanistic interpretation of the fragmentation of the carbenium ions produced by charge inversion of the enolate ions is unjustified because, in each case, more than one enolate ion probably is produced and the proportions of the differing ions is not known.

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