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Fragmentation Reactions of the Enolate Ions of 2-Pentanone

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The reaction of $[OH]^-$ with 2-pentanone produces two enolate ions, $[CH_3CH_2CH_2COCH_2]^-$ and $[CH_3COCHCH_2CH_3]^-$, by proton abstraction from C(1) and C(3), respectively. Using deuterium isotopic labelling the fragmentation reactions of each enolate have been delineated for collisional activation at both high (8 keV) and low (5–100 eV) collisional energies. The primary enolate ion fragments mainly by elimination of ethene. Two mechanisms operate: elimination of C(4) and C(5) with hydrogen migration from C(5), and elimination of C(3) and C(4) with migration of the C(5) methyl group. Minor fragmentation of the primary enolate also occurs by elimination of propane and elimination of C_2H_5; the latter reaction involves specifically the terminal ethyl group. The secondary enolate ion fragments mainly by loss of H_2 and by elimination of CH_4; for the latter reaction four different pathways are operative. Minor elimination of ethene also is observed involving migration of a C(5) hydrogen to C(3) and elimination of C(4) and C(5) as ethene.

INTRODUCTION

Over the past 15 years there has developed considerable interest in the analytical use of negative ion mass spectrometry, particularly in the areas of negative ion chemical ionization[1–3] and negative ion fast atom bombardment.[4,5] These soft ionization techniques usually yield ions characteristic of the relative molecular mass of the compound of interest but often do not produce the fragment ions which are necessary to derive structural information. Collision-induced dissociation (CID) of polyatomic ions has proven[6] to be a powerful method to provide such structural information and, as a consequence, there is a continuing interest in the collision-induced fragmentation reactions of gaseous ions. In addition to the analytical uses, fundamental information concerning the behaviour of gaseous ions can be derived from such collisional activation studies.[4,7]

The reaction of gaseous Brønsted bases with carbonyl compounds produces enolate negative ions[1,2] and there has been considerable interest in the fragmentation reactions of such species derived from ketones[8–19] and esters.[10,11,19–24] The present work extends these studies to the case of 2-pentanone, one of the simplest ketones which can form two enolate ions, $[CH_3CH_2CH_2COCH_2]^-$ and $[CH_3COCHCH_2CH_3]^-$. Using deuterium labelling the fragmentation reactions of these two enolate ions have been delineated both following activation by 8 keV collisions, using the mass-analyzed ion kinetic energy (MIKE) spectrometric technique,[25] and as a function of collision energy (and, hence, internal energy) using the technique of energy-resolved mass spectrometry (ERMS).[26–28] These enolate ions also are the simplest which show elimination of ethene, a reaction first observed by Hunt and colleagues.[11,12] Following the commencement of the present work, Bowie and co-workers have reported the observations of ethene elimination from the enolate ions of 4-heptanone,[14] 3-ethyl-2-pentanone[15] and 3,3-dimethylheptane-4-one[17] and have proposed several distinct mechanisms based on extensive isotopic labelling. The present work supports and extends these results.

EXPERIMENTAL

All experiments were carried out using a VG Analytical ZAB-2FQ mass spectrometer, which has been described previously.[29] Briefly, the instrument is a reversed-geometry double-focusing mass spectrometer with a third stage consisting of a deceleration lens system, an r.f.-only quadrupole collision cell and a quadrupole mass analyzer. In the low-energy collisional experiments the appropriate ions were mass-selected by the double-focusing *BE* instrument at 8 keV ion energy, decelerated to the appropriate collision energy (5–100 eV, laboratory scale) and introduced into the quadrupole where they underwent collision with N_2. The ionic fragmentation products were mass analyzed by the final quadrupole. The pressure of N_2 was $\sim 1.5 \times 10^{-7}$ Torr as indicated by an ionization gauge attached to the pumping line from the quadrupole section. For the high-energy collisional experiments, the ions of interest were selected by the magnetic sector and underwent collision, at 8 keV collision energy, with He in the second collision cell located between the magnetic and electric sectors. The ionic fragmentation products were analyzed according to their kinetic energy by scanning the voltage applied to the electric sector, the so-called

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MIKE spectrometric technique.[25] The He pressure, as measured by the ionization gauge on the pumping line for the region, was ~1.5 × 10^{-7} Torr. Unimolecular metastable ion fragmentation reactions occurring in the drift region between the magnetic and electric sectors were determined by the MIKE spectrometric technique in the absence of He gas in the collision cell. The enolate ions were prepared by reaction of the appropriate ketone with $[OH]^-$ in a chemical ionization source operating at ~200 °C and 50 eV ionizing electron energy. The $[OH]^-$ was prepared by electron impact on a 10% N_2O–90% CH_4 mixture. 2-Pentanone was a commercial sample of high purity. 2-Pentanone-1,1,1,3,3-d_5 was obtained from MSD Isotopes, Montreal. 2-Pentanone-1,1,1-d_3 was prepared by the Grignard reaction of CD_3MgI with butanal followed by oxidation of the resulting alcohol with pyridinium dichromate in dichloromethane.[30] 2-Pentanone-5,5,5-d_3 was prepared by the reaction of CD_3MgI with methyl vinyl ketone according to the method of Johnson and Marren.[31] Final purification was achieved by gas chromatography.

RESULTS AND DISCUSSION

The reaction of $[OH]^-$ with 2-pentanone produces abundant $[M-H]^-$ ions. The reaction with 2-pentanone-1,1,1,3,3-d_5 produced only $[M-D]^-$ ions, as expected, since positions 1 and 3 are the two acidic sites in 2-pentanone. By comparison with known acidities,[32] the $\Delta H^{\circ}_{\mathrm{acid}}$ of the two positions would not be expected to differ greatly; in agreement, the reaction of $[OH]^-$ with 2-pentanone-1,1,1-d_3 produced $[M-D]^-$ and $[M-H]^-$ ions in the ratio 56:44. Allowing for possible isotope effects this result indicates essentially statistical abstraction of H^+ from positions 1 and 3.

The 8 keV CID mass spectra for the enolate ions studied are presented in Fig. 1 in bar graph form. The major fragmentation reactions of the enolate ions derived from 2-pentanone (a) involve elimination of CH_4 and C_2H_4, with a metastable peak being observed for the latter reaction. Minor reactions involve elimination of H, H_2 and C_2H_5 and formation of $[HCCO]^-$ (*m/z* 41). The CID mass spectrum of the enolate ions, $[M-D]^-$, derived from 2-pentanone-1,1,1,3,3-d_5, show (b) that the ethene lost contains, for the most part, hydrogens from C(4) and C(5) only. Similarly, the ethyl group lost consists of the terminal ethyl group. By contrast methane is lost as CD_4, CH_3D and CH_4, while D/H_2 and HD also are eliminated. A metastable peak was observed for the reaction leading to elimination of C_2H_4.

More specific information comes from the CID mass spectra (Fig. 1(c) and (d)) of the primary enolate, $[M-D]^-$, and the secondary enolate, $[M-H]^-$, derived from 2-pentanone-1,1,1-d_3. The major fragmentation of the primary enolate ion involves elimination of C_2H_4 (a metastable peak was observed). The CID mass spectrum (e) of the $[M-H]^-$ ions of 2-pentanone-5,5,5-d_3 shows that, for the most part, this ethene elimination reaction involves hydrogen transfer from position 5, as illustrated in reaction (1), Scheme 1. A similar fragmentation sequence has been reported by Bowie and colleagues for the fragmentation of the enolate ion derived from 4-heptanone,[14] the primary enolate ion derived from 3-ethyl-2-pentanone,[15] and the enolate ion derived from 3,3-dimethyl-4-heptanone;[17] evidence has been presented in these papers that the reaction is stepwise. The secondary enolate ion, $[M-H]^-$, from 2-pentanone-1,1,1-d_3 also exhibits a minor peak in the CID spectrum (d) corresponding to C_2H_4 elimination (no metastable peak observed). The reaction occurring presumably is reaction (2) (Scheme 1); a similar reaction has been reported for the enolate ion derived from 3,3-dimethyl-4-heptanone.[17] A third pathway for elimination of ethene is revealed by the observation of a low-intensity peak at *m/z* 60 (loss of C_2H_4) in the CID mass spectrum of the enolate ions of 2-pentanone-5,5,5-d_3 (e). This ion incorporates the C(5) methyl group and pre-

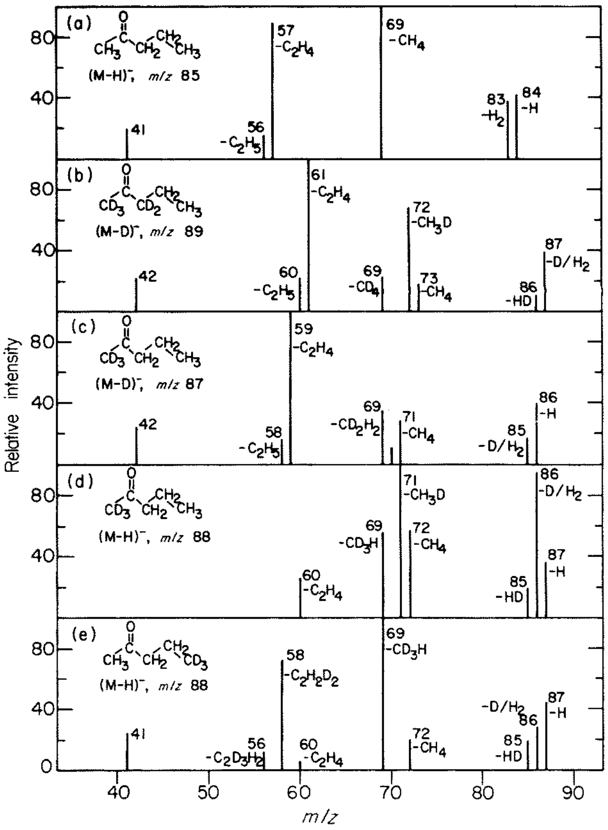
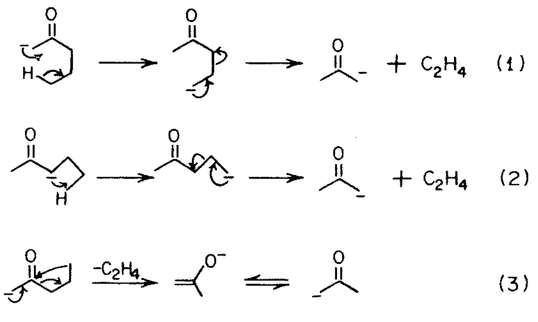
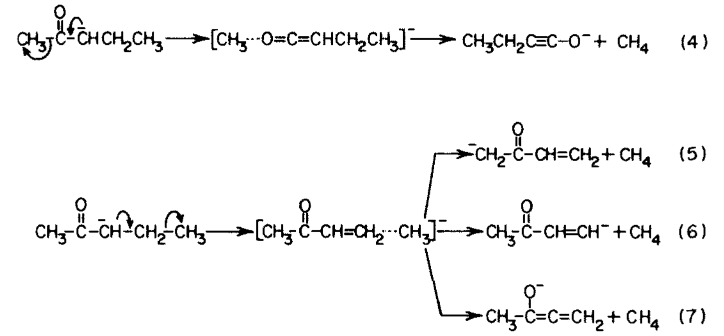


Figure 1. 8 keV CID mass spectra of enolate ions.



Scheme 1

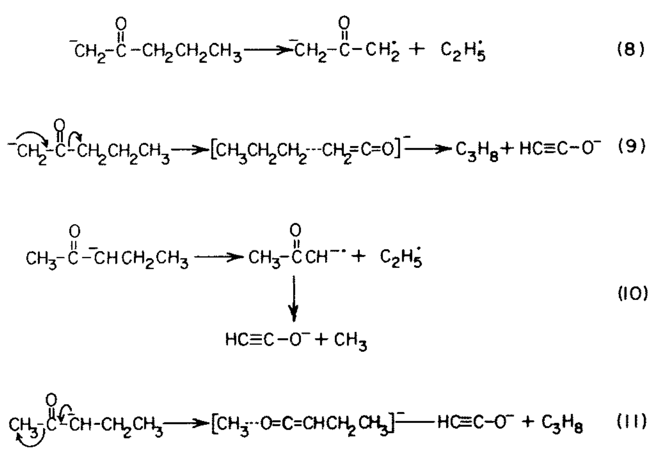


Scheme 2

sumably arises by reaction (3) (Scheme 1). A similar reaction has been proposed to rationalize the elimination of C_4H_8 from the primary enolate ion derived from 3-ethyl-2-pentanone[15] and the elimination of C(2) and C(3) as ethene in the fragmentation of the enolate ion of 4-heptanone.[14]

The major fragmentation reaction of the secondary enolate ion involves elimination of methane, and four routes appear to be involved, as illustrated in Scheme 2. Reaction (5) leads to CH_3D elimination from $[CD_3COCHCH_2CH_3]^-$ (Fig. 1(d)) and is the single most important reaction. Reaction (4) leads to CD_3H elimination in the spectrum in (d). Reaction (6) is indicated by the elimination of CH_4 from the $[M - D]^-$ ion derived from 2-pentanone-1,1,1,3,3-d_5 (b). There is no direct evidence for reaction (7) from the present work; however, Bowie *et al.*[17] have observed a similar reaction in the fragmentation of the enolate ion of 3,3-dimethyl-2-pentanone. The primary enolate ion shows minor loss of methane as shown by the ion signals at *m/z* 69, 70 and 71 in (c). The mechanism or mechanisms of these elimination reactions are not clear and may involve prior rearrangement of the primary enolate ion to the secondary structure. There is a precedent for such a rearrangement process.[16]

The results of Fig. 1 show that ethyl radical elimination occurs primarily for the primary enolate ion (but see the low-energy collision results below) and involves specific elimination of the terminal ethyl group, reaction (8) (Scheme 3). A similar specific elimination of an ethyl radical has been reported[14] in the fragmentation of the enolate ion of 4-heptanone. Elimination of propane (reaction (9)) also is observed only for the primary enolate ion and is directly analogous to elimination of CH_4 by reaction (4) for the secondary enolate ion. Because of the coincidence of the peaks corresponding to elimination of D and H_2 no definitive conclusions may be reached concerning the reactions leading to elimination of a hydrogen atom and a hydrogen molecule.



Scheme 3

Energy-resolved collisional studies

Collisional dissociation mass spectra of the $[M - H]^-$ ions of 2-pentanone, the $[M - D]^-$ ions of 2-pentanone-1,1,1,3,3-d_5 and the $[M - D]^-$ and $[M - H]^-$ ions derived from 2-pentanone-1,1,1-d_3 were obtained at center-of-mass collision energies up to 25 eV. The resulting breakdown graphs are shown in Figs 2–5. It was observed that the extent of fragmentation, following collisional activation, was considerably smaller for the secondary enolate ion

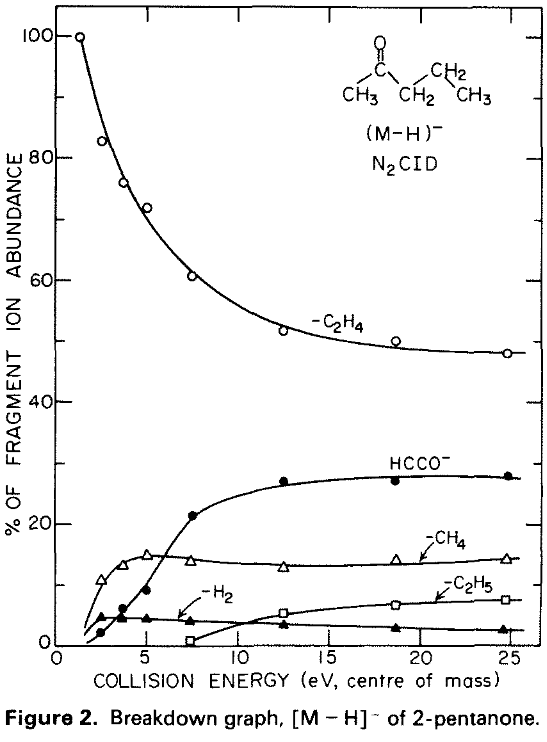


Figure 2. Breakdown graph, $[M - H]^-$ of 2-pentanone.

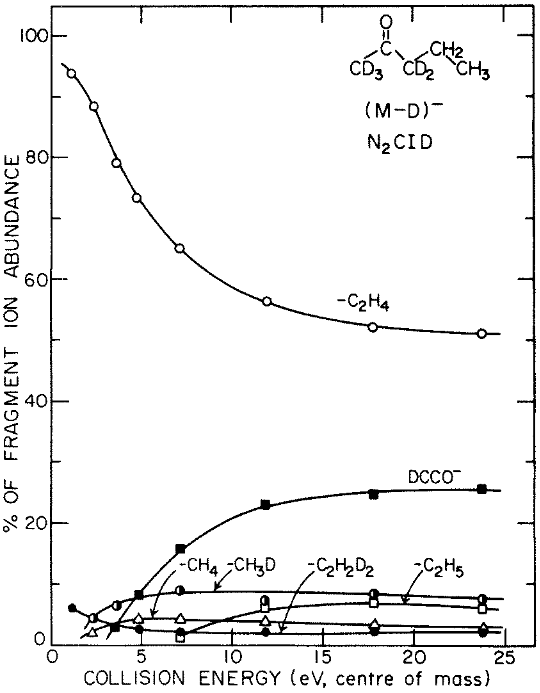


Figure 3. Breakdown graph, [M − D]⁻ of 2-pentanone-1,1,1,3,3-d_5.

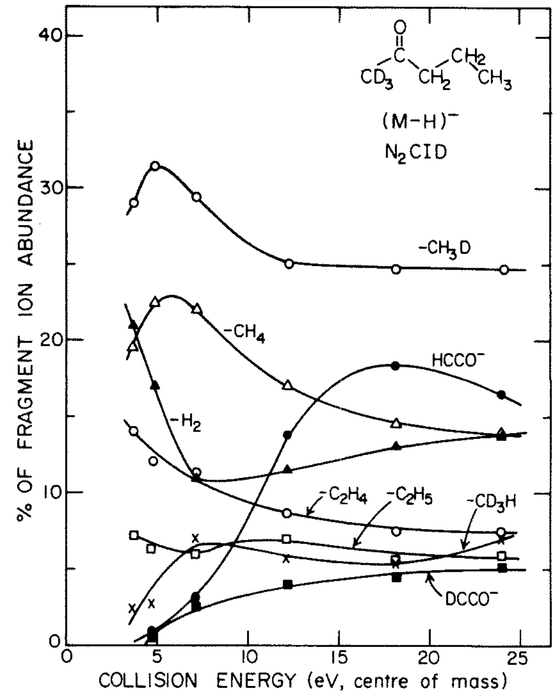


Figure 5. Breakdown graph, [M − H]⁻ of 2-pentanone-1,1,1-d_3.

$[CD_3COCHCH_2CH_3]^-$ than for the primary enolate ion $[CH_3CH_2CH_2COCD_2]^-$; consequently, the breakdown graphs of Figs 2 and 3 represent mainly, but not completely, fragmentation of the primary enolate ion.

Clearly, for the primary enolate ion, the most favorable reaction energetically is elimination of ethene, reaction (1); indeed, in all cases where the primary enolate ion was studied alone or in a mixture a metastable peak was observed for this reaction. Of particular interest is the observation (Fig. 3) of an ion signal corresponding to elimination of $C_2H_2D_2$ and indicating the occurrence of reaction (3). This reaction was not clearly detected in the high-energy CID spectrum because of the limited mass resolution of the MIKE spectrometric technique. In low-energy collisional activation elimination of methane from the primary enolate ion is of only very minor importance, the only other significant reactions being elimination of C_3H_8 (reaction (9)) and of C_2H_5 (reaction (8)); the latter reaction clearly has a high threshold energy.

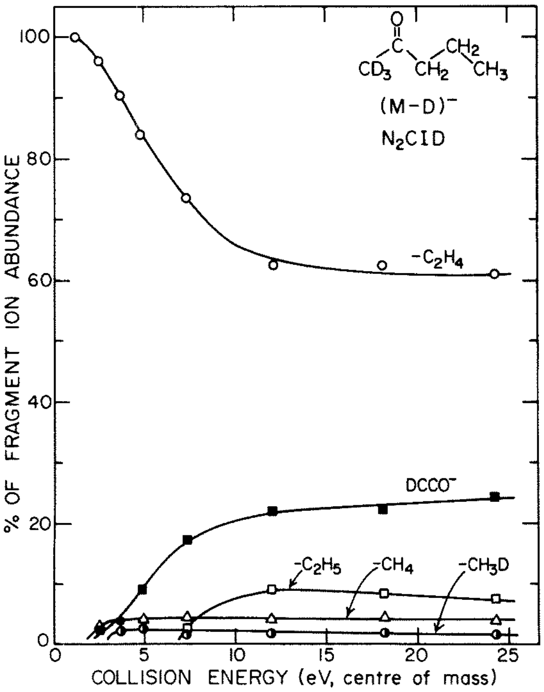


Figure 4. Breakdown graph, [M − D]⁻ of 2-pentanone-1,1,1-d_3.

Using thermochemical data, summarized in the Appendix, we derive reaction enthalpies of 95 kJ mol^{-1} for both reaction (1) and reaction (9), although the latter reaction clearly has the higher onset energy. We do not anticipate any activation barrier for reaction (1) beyond the reaction endothermicity. By contrast, reaction (9) proceeds through formation of a high-energy ion–dipole complex leading to a critical reaction energy greater than the reaction endothermicity.

In contrast to the primary enolate ion, no single ion dominates the breakdown graph of the secondary enolate ion (Fig. 5). The lowest collision energy for which detectable fragmentation was observed was ~3.6 eV center of mass (15 eV, laboratory scale). At this collision energy elimination of H_2, CH_3D, CH_4, CD_3H, C_2H_4 and C_2H_5 all are observed. Elimination of C_2H_5 (reaction (10), Scheme 3) is an unexpected reaction; however, the resulting radical anion is a stable species which, for example, is formed by reaction of $O^{-\bullet}$ with CH_3COCH_3.[33,34] This reaction may be occurring following 8 keV collisional activation but could not be clearly delineated because of the limited mass resolution in MIKE spectra. A particularly surprising product is $[HCCO]^-$, which becomes a prominent ion at higher collision energies. This product may result from further fragmentation of the $[CD_3COCH]^{-\bullet}$ ion formed in reaction (10) or it may originate by direct elimination of $CD_3C_2H_5$ from the secondary enolate ion (reaction (11)). This product was not observed in the high-energy CID experiments, possibly because the internal energy achieved by the fragmenting ions is lower in the high-energy collisional experiments.[24,35]

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APPENDIX

Assuming the gas-phase acidity of the 1-position of 2-pentanone is the same as that of acetone (1544 kJ mol^{-1})[32] we derive $\Delta H_f°$ ($[CH_3CH_2CH_2COCH_2]^-$) = -246 kJ mol^{-1}. From gas-phase acidity data $\Delta H_f°$ ($[CH_3COCH_2]^-$) = -203 kJ mol^{-1} and $\Delta H_f°$ ($[HCCO]^-$) = -51 kJ mol^{-1} have been derived,[36] while $\Delta H_f°$ (C_2H_4) = 52 kJ mol^{-1}[37] and $\Delta H_f°$ (C_3H_8) = -100 kJ mol^{-1}.