We found that the chemistry of acetylene exposed to these three catalysts is similar. high-mass C_nH_m species appear in the mass spectra that are characteristic of polymers containing mixtures of single, double, and triple bonds. The formation of large polymers, with only single and double bonds, does not appear to be very significant. The dramatic decrease in the Raman intensity correlates with desorption products producing mass spectra characteristic of acetylene trimers. It therefore appears that a trimer species may be responsible for the Raman spectrum.

This correlation of the Raman signal with a trimer appears to conflict with previous assignments of such a spectrum to a $\sigma_2\pi$-C_2H_2 rhodium-bonded moity or to a C_{30} polyene. Since our experimental conditions differ from those used in the previous work, a higher background pressure in one case and the presence of Rh on the alumina in the other, it is possible that different species produce similar Raman spectra in the three cases. On the other hand, it is not clear why the difference in background pressure should have a dramatic chemical effect for the high acetylene pressures being used. Also, the chemistry of acetylene exposed to thermally activated Al_2O_3 and to Rh/Al_2O_3 is similar, and the formation of polyenes on Al_2O_3 or Rh/Al_2O_3 appears not to be very significant. We therefore prefer to think that the same chemical species is responsible for the Raman spectra in the three cases. Differences in the observed frequencies can be attributed to differences in the binding site and strength of binding caused by differences in the experimental conditions.[12] More characteristics of the surface-bound species are needed, however, for a positive identification.

Because of the simplicity of the Raman spectrum and the complexity of the mass spectra that we obtained (see Figure 2), the general use of Raman spectroscopy by itself as a surface-sensitive probe under these experimental conditions appears to be limited. The experimental conditions produce several chemical species, and additional data are needed to correlate particular species with Raman spectra that are observed. On the other hand, an enhancement of the Raman scattering may selectively reveal chemically significant intermediates on the surface.

Acknowledgment. Professor A. Ueno of Toyohashi University of Technology is gratefully acknowledged for his assistance and advice.

Registry No. C_2H_2, 74-86-2; Al_2O_3, 1344-28-1; Rh, 7440-16-6.

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[12] α-Alumina was used in the work reported in ref 1. R. M. Hexter, private communication.

Carbanion Rearrangements. Collision-Induced Dissociations of the Enolate Ion of Heptan-4-one

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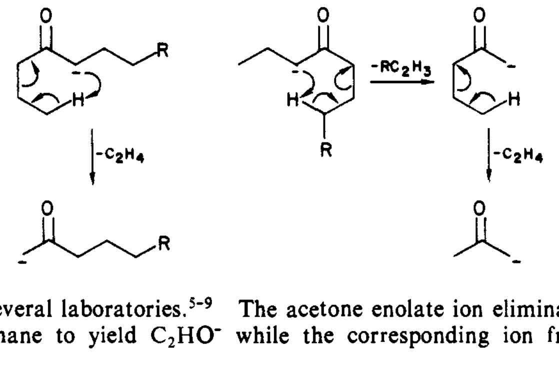
Contribution from the Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia 5001, and Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4, Canada. *Received November 26, 1985*

Abstract: The mechanisms of formation of the major negative ions produced in the collision-induced fragmentations of the enolate ion of heptan-4-one have been studied by using a series of D- and ^{13}C-labeled compounds. H atom loss is specific, involving position 3 (relative to the enolate position, 5). Methane elimination, the most abundant collision-generated fragment ion, largely involves the 1(7)CH_3 group together with a hydrogen atom from C-3(5). It was concluded from ^{13}C and D isotope effects that this reaction is stepwise with two kinetically significant steps. A minor methane loss (ca. 10%) involves H from C-6(2). C_2H_4 loss is also an important process, occurring for the most part (>90%) by loss of the ethyl group with a concomitant γ-hydrogen transfer to the anionic carbon or to oxygen, producing the $CH_3CH_2CH_2COCH_2^-$ and $CH_3CH_2CHC(OH)CH_2^-$ anions. Again, isotope effects show that the reaction must be stepwise. An unusual minor C_2H_4 loss is also observed involving specifically the elimination of a C2, C3 ethene unit, a reaction which must involve a methyl migration. Other decompositions are as follows: Loss of H_2 proceeds by two mechanisms, the first involving the 5 and 6 positions and the second the 1 and 2 positions. Elimination of $C_2H_5^{\bullet}$ is specific, producing $^{\bullet}CH_2COCH^-C_2H_5$. Loss of C_3H_8 occurs by two mechanisms, viz., loss of C_3H_7 from positions 5, 6, and 7 together with a hydrogen from position 3, with the second loss involving the methyl and ethyl groups at positions 1 and 6, 7, respectively.

In the past decade there have been significant advances in the analytical applications of negative ion mass spectrometry, particularly in the areas of negative ion chemical ionization and fast atom bombardment.[1] These "soft ionization" techniques often give molecular weight information, but in general, negative ions fragment but little and so, in many cases, fragment ions which in principle could yield structural information are absent from the spectra. Collision-induced dissociation of polyatomic negative ions can often provide this structural information.[1,2] In addition, fundamental information concerning ion behavior may be obtained from such studies.[1,3]

Enolate negative ions may be produced from alkyl ketones by reaction with HO^- in a chemical ionization source.[4] Collision-induced fragmentations of such enolate ions have been explored in several laboratories.[5-9] The acetone enolate ion eliminates methane to yield C_2HO^- while the corresponding ion from

Scheme I



[†] University of Adelaide.

[‡] University of Ottawa.

[1] Bowie, J. H. *Mass Spectrom. Rev.* **1984**, *3*, 161.

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Table I. CA Mass Spectra of Enolate Anions Derived from I–X Losses of H$^•$, H_2, CH_4, and C_2H_4

	loss (relative abundance)											
compd	H$^•$	D$^•$	H_2	HD	CH_4	$^{13}CH_4$	$^{13}CH_3D$	CD_3H	CH_3D	C_2H_4	$^{12}C^{13}CH_4$	$C_2H_2D_2$
I	18		54		100					48		
II	21		67		100						73	
III	23		63		100					21	21	
IV	43		100		83	75				46	42	
V		98^a	98^a	43	23	100^b	76		100^b	65	75^c	
VI		66^a	66^a	28	21				100	76		
VII	28			34	100				6			73
VIII	29		53^d	25	100					26.0		25.8
IX	28		43^e	23				100		2		40
X	81		92	21	100			85		50		28

^{a}Loss of 2 amu = D and/or H_2. ^{b}m/z 100 corresponds to the losses of $^{13}CH_4$ and CH_3D. ^{c}m/z 88 corresponds to the losses of $^{12}C^{13}CH_4$ and $C_2H_5^•$. ^{d}Since no D$^•$ is lost from VII, loss of 2 amu from VIII must be H_2. ^{e}Since there is no loss of H$^•$ from V or VI, loss of 2 amu from IX and X must be H_2.

Table II. CA Mass Spectra of Enolate Anions Derived from I–X Losses of $C_2H_5^•$ and C_3H_8

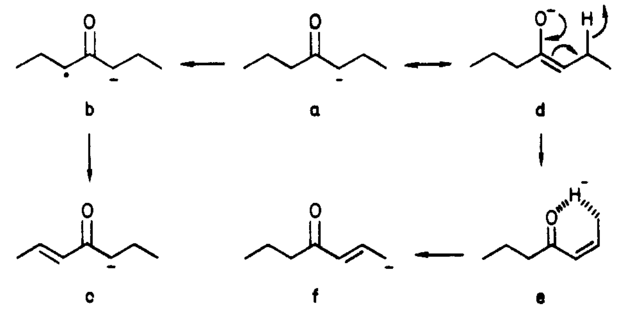
	loss (relative abundance)									
compd	$C_2H_5^•$	$^{12}C^{13}CH_5^•$	$C_2H_3D_2^•$	$C_2H_2D_3^•$	C_3H_8	$^{12}C_2{}^{13}CH_8$	$^{12}C_2{}^{13}CH_5D_3$	$C_3H_6D_2$	$C_3H_5D_3$	$C_3H_2D_6$
I	~6^a				10					
II		~5^a				12				
III	*b*	*c*			4	4				
IV	*d*	*e*			3	5				
V	75^f	~5^a				11	6		8	
VI	~6^a				6				4	
VII			~5^a					13		
VIII	*g*		*h*		5			4.5		
IX				7.5					7.5	3.5
X	*k*			7	8				16	

^{a}Not resolved. ^{b}Abundance should be the same as *c*. ^{c}Not resolved, 3%, small tail on low mass end of peak corresponding to elimination of $^{12}C^{13}CH_4$. ^{d}Abundance should be the same as *e*. ^{e}Not resolved, 5%, small tail on low mass end of peak corresponding to loss of $^{12}C^{13}CH_4$. ^{f}m/z 88 corresponds to the losses of $^{12}C^{13}CH_4$ and $C_2H_5^•$. ^{g}Abundance should be the same as *h*. ^{k}Not resolved, 2%, small tail on low mass end of peak corresponding to loss of $C_2H_2D_2$.

1,1,1-trifluoroacetone forms both C_2HO^- and CF_3^-.[5,6] The collisional activation (CA) mass spectra of a number of alkyl ketone enolate ions have been described by Hunt and colleagues.[7,8] Rearrangement peaks in these spectra were ascribed to the six-center processes shown in Scheme I. These representations are in accord with the spectra of deuteriated derivatives (CD_2COCD_2).

We have reported that the loss of C_2H_4 from the butyrophenone $(M - H^+)^-$ ion produces the acetophenone enolate ion $PhCOCH_2^-$ but the reaction is very complex.[9] The carbons lost are those of the terminal ethyl group, but every hydrogen atom in the ion is involved through specific hydrogen rearrangements. This unusual result prompted the present detailed investigation of the CA mass spectrum of a dialkyl ketone enolate anion. The symmetrical system heptan-4-one was chosen, and a number of ^{13}C- and D-labeled derivatives were prepared to aid the study. The aims of the investigation were twofold: (i) to determine whether the rearrangement reactions are mechanistically simple (e.g., as shown in Scheme I), or whether they are more complex and involve atom scrambling, and (ii) to establish whether the rearrangements are simple six-center reactions and to use ^{13}C and D isotope effects to determine whether such processes are stepwise or concerted.

Scheme II



Results and Discussion

All collisional activation (CA) and charge exchange mass spectra reported in this paper were measured with a Vacuum Generators ZAB-2F mass spectrometer operating at 70 eV in the negative chemical ionization mode.[10] Water was used to produce HO^- reactant ions,[11,12] and helium was used as collision gas. Full details are provided in the Experimental Section. The compounds used are listed on the next page.

The major features of the CA mass spectra of the enolate anions derived from I–X are recorded in Tables I and II. Of these, the most informative is that of IX, and this spectrum is shown in Figure 1. The data in Tables I and II and Figure 1 demonstrate a number of processes, all of which are specific. *No carbon or hydrogen scrambling precedes or accompanies any decomposition.*

(1) The Losses of H$^•$ and H_2. The losses of one and two hydrogen atoms from ion a are shown in Scheme II. The loss

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(12) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Szulejko, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 521.

$C_3H_7COC_3H_7$
I
$CH_3{}^{13}CH_2CH_2COCH_2{}^{13}CH_2CH_3$
II
$C_3H_7COCH_2{}^{13}CH_2CH_3$
III
$C_3H_7COCH_2CH_2{}^{13}CH_3$
IV
$CH_3CH_2CD_2COCD_2CH_2{}^{13}CH_3$
V
$CH_3CH_2CD_2COCD_2CH_2CH_3$
VI
$CH_3CD_2CH_2COCH_2CD_2CH_3$
VII
$C_3H_7COCH_2CD_2CH_3$
VIII
$CD_3CH_2CH_2COCH_2CH_2CD_3$
IX
$C_3H_7COCH_2CH_2CD_3$
X

of the first hydrogen atom is specific, producing resonance stabilized radical anion b. There are two competing eliminations of H_2, and since there are pronounced deuterium isotope effects for the reactions, it is not possible to determine the proportion of each process. The first can proceed through b to c, because the elimination involves hydrogens at the 2(6) and 3(5) positions. The second process is a 1,2(6,7) elimination of hydrogen: we represent this by the sequence d → f. This reaction is directly analogous to the stepwise 1,2 eliminations of alkoxides which proceed through solvated hydride (or alkyl) ion intermediates.[13,14]

(2) The Elimination of Methane. The elimination of CH_4 from the heptan-4-one enolate anion produces the most abundant peak in the CA mass spectrum (Table I). The peak is of Gaussian type with no fine structure and has a width at half-height of 56 V which corresponds to an energy release of 0.20 eV. *There are two specific processes.* The minor process involves loss of the 1(7) methyl group and a 5(3) hydrogen atom. The spectrum of the D_6 derivative IX shows a clean loss of CD_3H showing that *no hydrogen exchange occurs between the 1 and 2 positions.* The respective CA mass spectra of VI and VII show the losses CH_3D:CH_4 = 100:21 and 6:100. There are different isotope effects operating in each case, but to a first approximation the mean of the two values gives a major to minor loss ratio of 100:13. The minor loss is unusual and poses a mechanistic problem, in that it was not possible to distinguish between the two possible mechanisms shown in Scheme III.

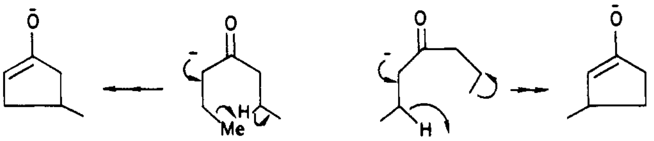
The major loss of methane occurs by the overall mechanism g → h (Scheme IV). The product is represented as the enolate ion h. Now the charge *reversal* mass spectra[15,16] of enolate negative ions R′–CO–CH$^-$–R show a characteristic elimination of RCH to produce R′CO$^+$.[9] The charge reversal spectra of both the parent ion (*m*/*z* 113) and the composite ion *m*/*z* 97 (ca. 90% h) are listed in Table III. Both spectra show the above characteristic fragmentation: for example, *m*/*z* 97 converts to a decomposing positive ion which forms i and C_3H_6 [see h → i (Scheme IV)].

We have measured D and ^{13}C isotope effects for reaction g → h using the D_2 and D_3 derivatives of heptan-4-one (produced by partial exchange of the α hydrogens of heptan-4-one with NaOD) and compounds IV and X. The observations are shown in formula XI (Scheme IV)—note that the minor loss of CH_4 (see Scheme III) will not affect these values.[17] The observation of a primary ^{13}C and secondary D isotope effect at C-1 together with the D isotope effect at H-5 can be interpreted in one of two ways. *Either the reaction is concerted or it is stepwise with two steps being kinetically significant.*

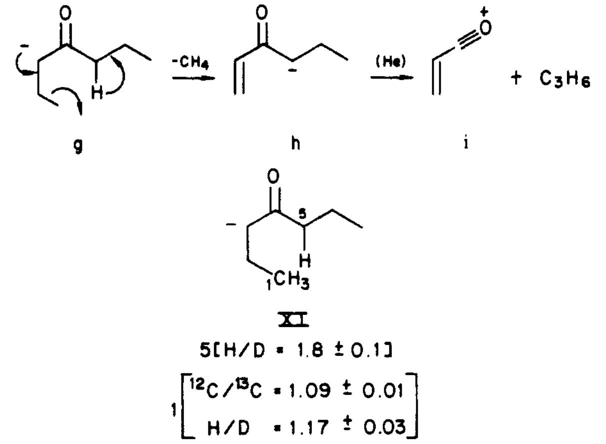
Table III. Charge Reversal Mass Spectra of Negative Ions *m*/*z* 113, 97, and 85 in the CA Mass Spectrum of the Heptan-4-one Enolate Anion

	Charge Reversal Fragment Cations [*m*/*z* (%) Composition]:
A. *m*/*z* 113: ($C_7H_{13}O^-$)	71 (24) $C_4H_7O^+$, 70 (16) $C_4H_6O^{\bullet+}$, 69 (12) $C_4H_5O^+$, 67 (5) $C_4H_3O^+$, 55 (100) $C_3H_3O^+$, 43 (98) $C_3H_7{}^+$, 41 (97) $C_3H_5{}^+$, 39 (53) $C_3H_3{}^+$, 29 (22) $C_2H_5{}^+$, and 27 (62) $C_2H_3{}^+$
B. *m*/*z* 97: ($C_6H_9O^-$)	97 (2) $C_6H_9O^+$, 96 (4) $C_8H_8O^{\bullet+}$, 95 (6) $C_6H_7O^+$, 79 (6) $C_6H_7{}^+$, 77 (4) $C_6H_5{}^+$, 70 (7) $C_4H_4O^{\bullet+}$, 69 (11) $C_4H_3O^+$, 55 (100) $C_3H_3O^+$, 53 (6) C_3HO^+, 41 (21) $C_3H_5{}^+$, 39 (21) $C_3H_3{}^+$, 29 (4) $C_2H_5{}^+$, and 27 (32) $C_2H_3{}^+$
C. *m*/*z* 85: ($C_5H_9O^-$)	71 (20) $C_5H_7O^+$, 70 (2) $C_5H_6O^{\bullet+}$, 69 (5) $C_5H_5O^+$, 68 (4) $C_5H_4O^{\bullet+}$, 67 (2) $C_5H_3O^+$, 55 (16) $C_3H_3O^+$, 54 (8) $C_3H_2O^{\bullet+}$, 53 (8) C_3HO^+, 43 (81) $C_3H_7{}^+$, 42 (100) $C_2H_2O^{\bullet+}$ and/or $C_3H_6{}^{\bullet+}$, 41 (71) $C_3H_5{}^+$, 39 (54) $C_3H_3{}^+$, 29 (28) $C_2H_5{}^+$, and 27 (52) $C_2H_3{}^+$

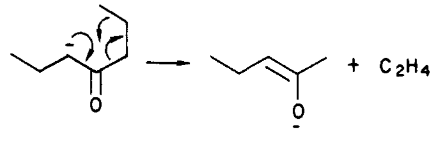
Scheme III



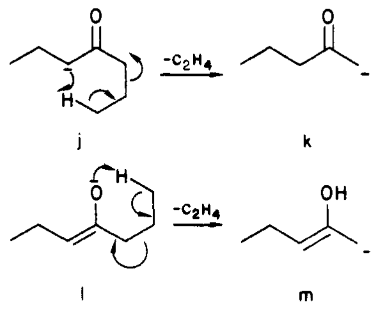
Scheme IV



Scheme V



Scheme VI



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(17) Even if the isotope effect for the minor process is 25% ($^{12}C/^{13}C$ = 1.25), the value for the major process will be 1.08, i.e., *within* the experimental error.

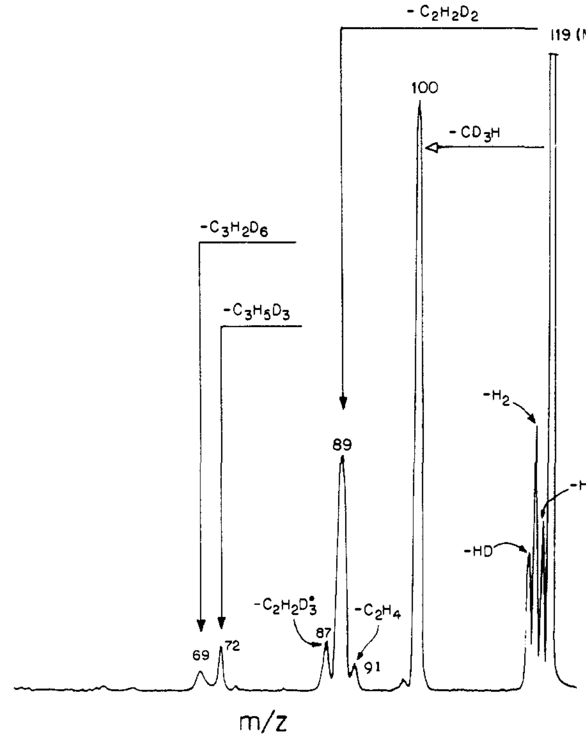


Figure 1. Collisional activation mass spectrum of the enolate ion of $(CD_3CH_2CH_2)_2CO$. For experimental details see the Experimental Section.

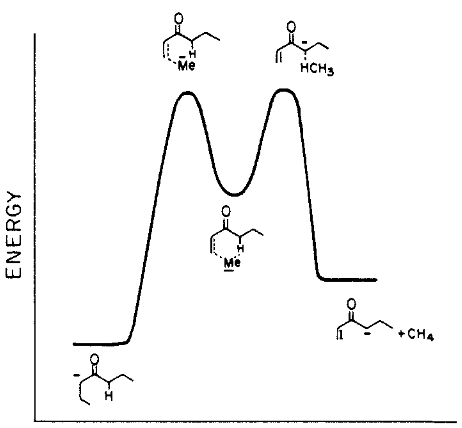
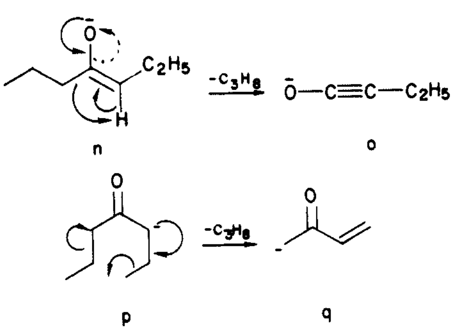


Figure 2. Mechanism proposed for the methane elimination g → h. Using Benson's additivity rules[20] and an electron affinity (EA) of $C_3H_7CO\dot{C}HC_2H_5$ = 1.72 eV[21] and assuming an EA of 2.06 eV for $CH_2{=}CHCO\dot{C}HC_2H_5$ (by analogy with EA($C_6H_5CO\dot{C}H_2$) = 2.06 eV[21]), ΔH_f for the overall process = +30 kJ mol^{-1}.

Gas-phase reactions which have two kinetically significant steps are rare, but examples have been reported.[13,14] Belasco, Albery, and Knowles[18] have described in the general case how it should be possible to identify such two-step reactions by double isotopic labeling. Consider the case of reaction g → h (Scheme IV). The primary ^{13}C isotope effect at C-1 is $^{12}C/^{13}C$ = 1.09 ± 0.01 and the D isotope effect at C-5 for the deprotonation is 1.8 ± 0.1. The $^{12}C/^{13}C$ ratios need to be compared for the enolate ions of IV and the ^{13}C, D_3 derivative V. If the reaction is stepwise as shown in Figure 2, the activation energy for the second process [removal of D^+ for V] will increase and the kinetic significance of step 1 will decrease, i.e., for V, $^{12}C/^{13}C < 1.09$. In contrast, if the reaction is concerted, there should be no change in the $^{12}C/^{13}C$ ratio, i.e., $^{12}C/^{13}C$ for both IV and V should be 1.09. The result of this experiment for $^{12}C/^{13}C$ for V is 1.00 ± 0.01.[19] *The reaction is therefore stepwise*, and the proposed mechanism is shown in Figure 2.

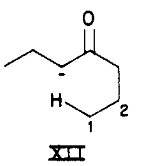
Scheme VII



(3) The Losses of C_2H_4 and $C_2H_5^•$ (Tables I and II). The CA mass spectrum of the D_6 derivative IX (Figure 1) best illustrates the various losses of $C_2H_5^•$ and C_2H_4. The spectrum shows losses of $C_2H_2D_3^•$, $C_2H_2D_2$, and C_2H_4 from m/z 119. All losses are specific and occur without carbon or hydrogen scrambling. The losses of $C_2H_5^•$ and H• [a → b (Scheme II)] from the heptan-4-one enolate ions are directly analogous: the structure of the product ion arising by loss of $C_2H_5^•$ is $^•CH_2COCH^-C_2H_5$. *There are two losses of C_2H_4* occurring in the ratio 100:8. The minor loss is again unusual, involving the specific elimination of a 2,3(5,6) CH_2CH_2 unit. *This reaction must involve a methyl anion migration.* A number of mechanistic proposals can be drawn, but most produce nonstabilized product anions. A possible mechanism is shown in Scheme V.

The major loss of C_2H_4 occurs by elimination of the terminal ethyl group together with a specific γ-hydrogen rearrangement, a process analogous to those proposed by Hung[7,8] (Scheme I). However, two plausible six-center processes may be drawn to rationalize this reaction, viz., j → k and l → m (Scheme VI). The product negative ions of the two proposed sequences are different, and the charge *reversal* mass spectrum of m/z 85 (Table III) shows loss of $:CH_2$ and so it is proposed that at least some of the product ions in Scheme VI have structure k. The preferred mechanism is j → k, but the possibility of some reaction through l or indeed conversion of m to k cannot be excluded.

The peak corresponding to loss of C_2H_4 in the CA mass spectrum of the heptan-4-one enolate anion has no fine structure, is steep sided with a rounded top, and is very wide. The width at half-height is 100 V, corresponding to an energy release of 0.42 eV. This is in keeping with a reaction having a reverse energy barrier. The value is very similar to that of 0.44 eV obtained for the loss of C_2H_4 from the butyrophenone enolate ion.[9] We estimate ΔH_f for the process f → k + C_2H_4 to be +94 kJ mol^{-1} on the assumption that the radical forms of f and k have the same electron affinity.



XIII

1 $\left[\begin{array}{l} ^{12}C/^{13}C = 1.10 \pm 0.01 \\ H/D = 1.81 \pm 0.02 \end{array}\right]$

2 $\left[\begin{array}{l} ^{12}C/^{13}C = 1.00 \pm 0.01 \\ H/D = 1.01 \pm 0.02 \end{array}\right]$

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[18] Belasco, J. G.; Albery, W. J.; Knowles, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2475.

[19] The measured ratio of m/z 99 ($-^{13}CH_3D$):100[$-(CH_3D + {}^{13}CH_4)$]:101($-CH_4$) = 77:100:23. The ^{13}C label in the 1 position causes the minor loss of CH_4 to be more favorable than in other spectra. If the $^{12}C/^{13}C$ ratio for the minor process is 1.00, the isotope effect $^{12}C/^{13}C$ for g → h is 1.00. If the $^{12}C/^{13}C$ ratio for the minor process is say 1.25 (a figure which, in our view, is an upper limit), the value for g → h is 1.055. A $^{12}C/^{13}C$ ratio of 1.44 for the minor process would be required to make the value for the major elimination of CH_4 be 1.09.

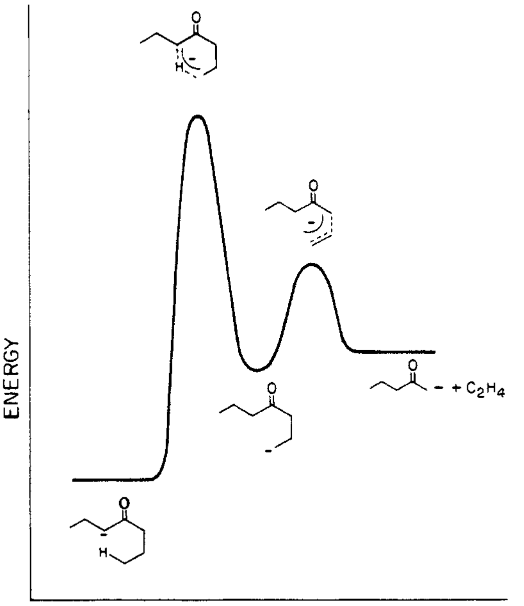

Figure 3. Suggested mechanism for the ethane elimination j → k.

The experimental values for ^{13}C and D isotope effects measured for the various eliminations of ethene [from compounds III, IV, VII, and IX] are shown alongside formula XII. It is not believed that the competing minor loss of C_2H_4 will affect these values. In this case, the message from the experimental isotope effects is clear and unambiguous; the reaction is stepwise, and it is the first step of the reaction which is rate determining. We represent this in qualitative terms for reaction g → k (Scheme VI) as shown in Figure 3.

(4) Formation of $C_4H_5O^-$ Ions. The ions $C_4H_5O^-$ are produced by two processes of comparable efficiency [e.g., Figure 1]. We cannot make a more quantitative statement concerning the ratios because isotope effects mask the true ratio. The first process, n → o (Scheme VII), is a standard reaction of enolate ions; corresponding reactions have been reported for the acetone[5,6] and butyrophenone[9] enolate anions. The peak for this reaction is of Gaussian type and is relatively narrow (28 V at half-height), corresponding to an energy release of 0.025 eV. The second reaction, p → q (Scheme VII) is quite unusual, involving elimination of a methyl from one side chain together with an ethyl from the other alkyl group, possibly via a six-center process. The peak for this process is also of Gaussian type and has a width at half-height of 49 V, corresponding to a kinetic energy release of 0.078 eV.

In conclusion: (i) The CA mass spectrum of the heptan-4-one enolate ion shows characteristic fragmentations which occur without carbon or hydrogen scrambling of the side chains. Such spectra of dialkyl ketones should therefore be suitable for structure determination purposes. (ii) The major fragmentation of the heptan-4-one enolate is elimination of methane through a six-center state. The process is two step with both steps being rate determining: this is the first report of the application of the double isotope labeling technique[18] in a gas phase ion reaction. (iii) The major elimination of ethene from the heptan-4-one enolate involves a γ-hydrogen rearrangement in which the first step (proton abstraction) is rate determining.

Experimental Section

Collisional activation and charge reversal mass spectra were recorded on a Vacuum Generators ZAB 2F mass spectrometer. All slits were fully open to obtain maximum sensitivity and to minimize energy-resolution effects.[20] The CI slit was used in the ion source, with ionizing energy 70 eV, trap current 100 μA, and ion source temperature 200 °C. The enolate negative ions from heptan-4-one and the labeled derivatives were generated by H abstraction by HO^- (or $H^- + O^{\bullet-}$) or D abstraction by DO (or $D^- + O^{\bullet-}$) reactant ions.[23,24] Reagent negative ions were produced by 70-eV electrons on H_2O or D_2O where appropriate.[7,25-27] The indicated source ion gauge pressure (of H_2O or D_2O) was ca. 2×10^{-6} Torr. The heptan-4-one pressure was typically 2×10^{-7} Torr. The *estimated* total pressure within the source is 2×10^{-2} Torr. The pressure of He in the second collision cell was 2×10^{-7} Torr, measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of ca. 10% and thus corresponded to essentially single collision conditions.

The Preparation of Compounds I–X. All labeled heptan-4-ones were first distilled at 80–90 °C (60 mmHg) with use of a small glass T tube. They were then subjected to GC separation on 20% SE-30 on Chromosorb AW 60–80 mesh (6 mm × 3 m) glass column, N_2 flow 50 mL/min at 185 °C. The retention time was 9.3 min under these conditions. The purity was either checked by ^1H or ^{13}C NMR, as appropriate, and the percentage incorporation of label was determined by positive ion mass spectrometry.

Heptan-4-one (I). (a) Ethyl 2-ethyl-3-oxohexanoate was prepared from ethyl 3-oxohexanoate by the method of Weider.[28] (b) Ethyl 2-ethyl-3-oxohexanoate (284 mg, 1.33 mmol) in aqueous sodium hydroxide (5%, 5 mL) was heated under reflux for 6.5 h, cooled to 20 °C, poured into water (15 mL), and extracted with diethyl ether (3 × 12 mL). The organic extract was washed with water (12 mL) and saturated aqueous sodium chloride (12 mL) and dried ($MgSO_4$). Removal of the solvent followed by distillation (see above) gave heptan-4-one (I) as a colorless liquid (79 mg, 52%).

(3,3,5,5-$^2H_4$)Heptan-4-one (VI) and (1-^{13}C-3,3,5,5-$^2H_4$)Heptan-4-one (V). Exchange of heptan-4-one (I) and (1-^{13}C)heptan-4-one (IV), respectively, with 2 N NaOD (10-fold excess) at 120 °C in a sealed tube for 2 h gave the required products VI and V as colorless oils in quantitative yield ($^2H_4$ = 95%, $^2H_3$ = 5%).

(2,2-$^2H_2$)Heptan-4-one (VIII). **(a) Ethyl 2-((1,1-$^2H_2$)ethyl)-3-oxohexanoate.** Ethyl 3-oxohexanoate (237 mg, 1.5 mmol) was added dropwise to a stirring solution of potassium (59 mg, 1.5 mmol) in anhydrous *tert*-butyl alcohol (4 mL), and the resultant mixture was stirred for 15 min at 20 °C. (1,1-$^2H_2$)Iodoethane (0.135 mL, 260 mg, 1.65 mmol) was added dropwise, and the mixture was heated under reflux for 3.5 h, poured into water (25 mL), acidified with aqueous hydrogen chloride (2 N), and extracted with diethyl ether (3 × 12 mL). The organic extract was washed with diethyl ether (3 × 12 mL). The organic extract was washed with water (12 mL), aqueous sodium hydrogen sulfite (20%, 12 mL), water (12 mL), saturated aqueous sodium chloride (12 mL), dried ($MgSO_4$), and distilled as described above to yield ethyl 2-((1,1-$^2H_2$)ethyl)-3-oxohexanoate[28] (283 mg, quantitative) as a yellow oil. (b) The above ester (283 mg) was treated as outlined for the synthesis of heptan-4-one (I). The residual oil gave (2,2-$^2H_2$)heptan-4-one (75 mg, 50%) as a colorless liquid ($^2H_2$ > 99%).

(1,1,1-$^2H_3$)Heptan-4-one (X). The synthesis is the same as that of VIII except that (2,2,2-$^2H_3$)iodoethane is used for the formation of ethyl 2-((2,2,2-$^2H_3$)ethyl)-3-oxohexanoate which is converted to (1,1,1-$^2H_3$)heptan-4-one (X) in 51% yield ($^2H_3$ > 99%).

(2,2,6,6-$^2H_4$)Heptan-4-one (VII). (a) Ethyl (5,5-$^2H_2$)3-Oxohexanoate. Ethyl acetoacetate (0.190 mL, 195 mg, 1.5 mmol) was added dropwise to a stirring suspension of sodium hydride (60% dispersion in oil, 72 mg, 1.8 mmol) in anhydrous tetrahydrofuran (3 mL) maintained at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 15 min, and *n*-butyllithium in hexane (1.0 mL, 1.6 M; 1.6 mmol) was added dropwise at 0 °C and stirred for 15 min. (1,1-$^2H_2$)Iodoethane (0.135 mL, 260 mg, 1.65 mmol) was added, the reaction mixture was stirred at 20 °C for 1.5 h, poured into water (20 mL), acidified with aqueous hydrogen chloride (2 N), and extracted with diethyl ether (3 × 12 mL). The organic phase was washed with water (2 × 12 mL) and saturated aqueous sodium chloride (12 mL), and dried ($MgSO_4$). The solvent was evaporated to give a yellow oil (263 mg) which contained the desired product together with 28 mg of oil from the sodium hydride suspension. (b) The crude ester was allowed to react with (1,1-$^2H_2$)iodoethane (0.135 mL, 360 mg, 1.65 mmol) [as for VIIIa above] to yield (1,1-$^2H_2$)ethyl

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2-((1,1-$^2H_2$)ethyl)-3-oxohexanoate as a yellow oil (quantitative yield). The ester was hydrolyzed and decarboxylated [as in the synthesis of heptan-4-one (I), above] to give (2,2,6,6-$^2H_4$)heptan-4-one in 60% yield ($^2H_4 > 99\%$).

(1,1,1,7,7,7-$^2H_6$)Heptan-4-one (IX). This synthesis uses the same procedures as that of VII above, except that in both steps (2,2,2-$^2H_3$)-iodoethane is used. The product (65 mg) was obtained as a colorless liquid ($^2H_6 > 98\%$).

(2,6-$^{13}C_2$)Heptan-4-one (ii). Preparation as for VII except that (1-^{13}C)iodoethane ($^{13}C = 91\%$) was used. Yield 53 mg.

(2-^{13}C)Heptan-4-one (III) and (1-^{13}C)Heptan-4-one (IV). Preparation as for VIII except that (1-^{13}C)iodoethane ($^{13}C = 91\%$) and (2-^{13}C)-iodoethane ($^{13}C = 91\%$) were used for III and IV, respectively. Yields 60 and 65 mg, respectively.

The Formation of the α-$^2H_1$ and α-$^2H_2$ Enolate Ions of Heptan-4-one. The ions [$MeCH_2\bar{C}HCOCD_2CH_2Me$ plus $MeCH_2\bar{C}DCOCHDCH_2Me$] and [$MeCH_2\bar{C}HCOCHDCHMe$ plus $MeCH_2\bar{C}DCOCH_2CH_2Me$] were produced by the reaction between DO^- and the partially labeled compounds produced by shaking heptan-4-one with a fourfold excess (by volume) of NaOD for 15 min at 20 °C. The DO^-/NICI Spectrum showed the following incorporations for enolate ions: $^2H_0 = 5\%$, $^2H_1 = 45\%$, $^2H_2 = 35\%$, and $^2H_3 = 15\%$.

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(p–d) π Bonding in Fluorosilanes? Gas-Phase Structures of $(CH_3)_{4-n}SiF_n$ with $n = 1$–3 and of t-Bu_2SiF_2

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Abstract: The gas-phase structures (r_g values) of the methylfluorosilanes $(CH_3)_{4-n}SiF_n$ with $n = 1$–3 and of di-*tert*-butyldifluorosilane, t-Bu_2SiF_2, have been determined by electron diffraction. In the case of CH_3SiF_3 the microwave rotational constant was included in the structure analysis. In the methylfluorosilane series a steady decrease of Si–F and Si–C bond lengths is observed with increasing fluorination: Si–F = 1.600 (2), 1.586 (2), and 1.570 (2) Å and Si–C = 1.848 (2), 1.836 (2), and 1.828 (4) Å for $(CH_3)_3SiF$, $(CH_3)_2SiF_2$, and CH_3SiF_3, respectively. These trends are rationalized by increasing polar contributions and contraction of the silicon valence shell. Ab initio calculations for SiF_4 indicate that (p–d) π bonding is negligible. Substitution of the methyl groups in $(CH_3)_2SiF_2$ by *tert*-butyl groups leads to lengthening of Si–F and Si–C bonds and strong variations in the silicon bond angles: Si–F = 1.586 (2), 1.606 (4) Å; Si–C = 1.836 (2), 1.869 (3) Å; CSiC = 116.7 (6)°, 125.5 (11)°; and FSiF = 104.6 (4)°, 97.7 (8)° in $(CH_3)_2SiF_2$ and t-Bu_2SiF_2, respectively.

The bonding properties in silicon compounds have attracted considerable interest for many years, because some properties of these compounds differ strongly from those of analogous carbon or germanium derivatives. Among these properties are structural features such as experimental Si–X bond lengths (see Table I), which are always shorter than the sum of the respective covalent radii. If polar effects due to electronegativity differences are taken into account, as suggested by Schomaker–Stevenson,[6] the prediction for the Si–C bond is very close to the experimental value, but Si–X bonds with more electronegative atoms X are still predicted to be too long. The difference increases monotonically with increasing electronegativity of X and amounts to 0.16 Å for the Si–F bond in SiF_4. It has been suggested that (p–d) π bonding would account for this difference, and this concept has been widely accepted.[7] It has helped to rationalize structural features of many silicon compounds (e.g., $(SiH_3)_3N$[2] and $(SiH_3)_2O$[3]). According to this concept the unoccupied Si 3d orbitals are contracted in the presence of electronegative ligands, and electron transfer from the lone pairs of N, O, or F into these empty orbitals results in effective (p–d) π back bonding. On the other hand, a crude consideration of bond energies (Table I) makes it unlikely that (p–d) π bonding is responsible for the high bond energy of Si–F bonds (135 kcal/mol). As suggested by Pauling[6] the σ bond energy for an A–B bond can be estimated from the geometric mean of the bonds A–A and B–B. The differences Δ between these estimated values and the actual bond energies are due to polar or π bonding contributions. In the case of the Si–C bond, the small difference of 10 kcal/mol can very well be due to a small

Table I. Si–X Bonds Lengths (in Å) and Bond Energies for X = C and F (in kcal/mol)

	exptl	cov. radii	S.S.[a]
Si–C in $Si(CH_3)_4$	1.875 (2)[b]	1.94	1.88
Si–N in $(SiH_3)_3N$	1.734 (3)[c]	1.87	1.81
Si–O in $(SiH_3)_2O$	1.634 (2)[d]	1.83	1.77
Si–F in SiF_4	1.553 (2)[e]	1.81	1.71
	Si–C in Me_4Si	Si–F in SiF_4	
E_b (exptl)[f]	70	135	
σ[g]	60	40	
Δ[h]	10	95	
polar contr.	10	100	

[a] Schomaker–Stevenson values. [b] Reference 1. [c] Reference 2. [d] Reference 3. [e] Reference 4. [f] Reference 5. [g] Geometric mean of Si–Si and X–X (X = C or F) σ bond energies. [h] $\Delta = E(\text{exptl}) - \sigma$.

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