Positive Ion and Neutral Fragment
Mass Spectrometry of Ketones

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Positive ion and neutral fragment
mass spectrometry of ketones

by

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ABSTRACT

Fragmentation patterns of twenty ketones are analyzed by positive ion and neutral fragment mass spectrometry. Appearance potentials and calculated heats of formation are used to characterize the positive ions. Ionization potentials and calculated heats of formation are used to characterize the neutral fragments. Neutral fragment mass spectra of twenty ketones and heats of formation for positive ions and neutral fragments are presented.

INTRODUCTION

Chemistry of Ketones

The chemistry of ketones in the mass spectrometer is known and has been well studied.^{1,2} Unimolecular decompositions are of greatest interest. Following the ionization of the parent molecule, activity centers about the carbonyl group and the chief reactions involve α -cleavage on either side of the carbonyl group, followed by fragmentation of both products; loss of CO; rearrangement; and γ -cleavage, including the McLafferty rearrangement.³

These reactions are summarized in Table 1, where the R groups are alkyl groups in which one carbon chain is at least three carbon atoms long, and such that $R_4 + C_2H_4 = R_2$ and A is an alkene one carbon shorter than R_2 .

This summary of reactions will serve as a guide to the possible species that may be encountered in the mass spectrometric study of ketones. It should be understood that further fragmentation of any product is possible and may lead to other detectable species. To illustrate, consider the ketone, 2-hexanone, molecular weight 100.

Table 1. Ketone Reactions⁴

$R_1COR_2^+$	$\longrightarrow$	$R_1 + R_2CO^+$	(α -fragmentation)
	$\longrightarrow$	$R_2 + R_1CO^+$	(α -fragmentation)
	$\longrightarrow$	$R_1COC_2H_4^+ + R_4$	(γ -fragmentation)
	$\longrightarrow$	$R_1COCH_3^+ + A$	(rearrangement)
	$\longrightarrow$	$R_1COH=CH_2^+ + A$	(McLafferty rearrangement)
R_2CO^+	$\longrightarrow$	$R_2^+ + CO$	(loss of CO)
	$\longrightarrow$	$C_2H_4CO^+ + R_4$	(γ -fragmentation)

The first reaction of 2-hexanone in the mass spectrometer will probably be ionization of the parent molecule. This should result in a peak in the mass spectrum of mass to charge ratio (m/z) 100. If cleavage then occurs at a position α - to the carbonyl group, there may be fragments at m/z 15 and 57, corresponding to CH_3^+ and $C_4H_9^+$, respectively. If the carbonyl-containing fragment retains the positive charge, peaks may appear at m/z 85 and 43, corresponding to $C_4H_9CO^+$ and CH_3CO^+ , respectively. The $C_4H_9^+$ species may fragment further into $C_2H_5^+$ and C_2H_4 , or to CH_3 and $C_3H_6^+$ or even to CH_2 and $C_3H_7^+$, giving rise to peaks at m/z 29, 28, 15, 42, 14 and 43.

Following the simple fragmentation involving α -cleavage, there may be two species with a carbonyl group: $C_4H_9CO^+$ (mass 85) and CH_3CO^+ (mass 43). Either one may lose the CO group, leaving additional $C_4H_9^+$ and CH_3^+ . Another possibility is that only part of the aliphatic chain may rupture, leaving, in the case of $C_4H_9CO^+$, $C_3H_7^+$ and CH_2CO . These processes may give rise to peaks at m/z 57, 15, 43 and 42.

The possibility of γ -site reaction exists only if one of the chains is at least three carbons long. In this case, a McLafferty rearrangement is possible and can be represented as

The mass spectrum of 2-hexanone may be expected to display prominent peaks at the following m/z ratios: 14, 15, 28, 29, 42, 43, 57, 58, 71, 85, and the parent, 100. The mass spectrum of 2-hexanone is displayed in Figure 9j. The only notable unexpected peak is due to m/z 27, and may be assumed to result from further fragmentation of the $C_4H_9^+$ into $C_2H_3^+$ and other products.

Mass Spectrometric Techniques

The identification of individual species in a mass spectrometer has become a relatively easy matter. In small molecules, where only one or two combinations of atoms to give a particular m/z ratio is possible, there is no guesswork. For instance, in the mass spectrum of a hydrocarbon, m/z 29 can be only $C_2H_5^+$. But if oxygen is also present in the compound, as in 2-hexanone, m/z 29 could also be CHO^+ . A high resolution mass spectrometer will readily resolve the dilemma,⁵ and will indeed give the relative amounts of each species. An alternative to the use of such an instrument is a check on the isotopic composition of certain pertinent ions. Suppose that m/z 43 could be either CH_3CO^+ or $C_3H_7^+$. Since ^{13}C accounts for ~1% of all carbon atoms, a mass 44 peak which is 2% as great as the mass 43 peak indicates CH_3CO^+ , while a 3% magnitude for the isotopic peak indicates $C_3H_7^+$. This method would not give the correct result if the m/z 44 peak was also caused by some other species, e.g., $C_3H_8^+$ or CO_2^+ in the above example.

More sophisticated methods of identification involve the detection of metastable ions. If an ion of mass m_1 and charge +1 decomposes in the field free region before the magnetic analyzer of a mass spectrometer, it may form a

neutral fragment and a daughter ion of mass m_2 and charge +1.

This process will be manifest in the mass spectrum as a diffuse peak of distinctive shape at $m/z = m_2^2 / m_1$.

For a given compound which has several possibilities for m_1 and m_2 , a metastable peak at a particular m/z will help to reduce the number of possible formulations for both ions. As an example, there is a metastable peak of m/z 40.0 in the spectrum of thiophene.⁶ The process is easily identified as:

The metastable peak identifies both the parent and the daughter ion, in this case m/z 84 and 58, although in this case, no formula other than $SC_2H_2^+$ is possible for m/z 58. Note that the pathway is also well defined. The daughter ion comes directly from the parent, not from some intermediary species. Thus fragmentation schemes may be studied as well, and pathways elucidated.

Appearance Potentials and Ionization Potentials

So far, the methods presented for identification of individual species have concerned themselves only with conventional ion mass spectra. That is, an electron beam of constant energy is used to fragment the molecules and the intensity of the ions resulting is plotted against the m/z ratio. If instead, the m/z ratio is held constant and the intensity of ions is plotted against electron energy, an ionization efficiency plot results. Using this method, the energy required to just cause the appearance of a given m/z ratio is measured.

The appearance potential (AP) of a given ion is defined as the energy required to produce the ion and its accompanying neutral fragment from a given molecule, and these species may or may not be in their ground states. The ionization potential (IP) of an ion is the energy required to remove only an electron completely from the atom or molecule in its ground state to form the ion, also in its ground state.⁷ This definition describes the adiabatic ionization potential, and assumes that reactants and products are in their ground state. Figure 1 is a potential energy diagram for the adiabatic ionization of a diatomic molecule. Note that the internuclear distance (r_e) may not remain constant for both the molecule and the molecular ion.

Figure 1. Adiabatic Ionization

A change in r_e requires at least one vibration, which will take about 10^{-13} sec. However, if ionization takes place in about 10^{-16} sec., there will be no time for a change in r_e , and an excited state of the molecular ion may be formed.⁸ Thus, the ionization potentials measured with a mass spectrometer may not be adiabatic, but instead vertical, and the products formed may be in their excited states. The effect of this excitation is a value for IP greater than the adiabatic IP by an amount corresponding to the extent of vibrational excitation in the ion. Figure 2 illustrates the vertical ionization process.

There are two cases to consider in these processes. The first is that of a parent molecule. Here the appearance potential is the ionization potential, the energy required to remove an electron from the molecule. As an example, consider the ionization of the simplest ketone, acetone.

The second case would be the appearance potential of a positive ion fragment from the parent; here, CH_3CO^+ .

Figure 2. Vertical Ionization

The energy required in Equation 1 is simply the ionization potential of the parent molecule. The energy required in the second and third equations is derivable from thermodynamics as

$$\begin{aligned}
 \Delta H_{\text{rxn}} &= \Delta H_f (\text{Products}) - \Delta H_f (\text{Reactants}) \\
 &= \Delta H_f (\text{CH}_3\cdot) + \Delta H_f (\text{CH}_3\text{CO}^+) + \Delta H_f (\text{CH}_3\text{COCH}_3^{+\bullet}) \\
 &\quad - \Delta H_f (\text{CH}_3\text{COCH}_3) - \Delta H_f (\text{CH}_3\text{COCH}_3^{+\bullet}) \\
 &= \Delta H_f (\text{CH}_3\cdot) + \Delta H_f (\text{CH}_3\text{CO}^+) - \Delta H_f (\text{CH}_3\text{COCH}_3)
 \end{aligned}$$

In this second process, both steps generally require energy, thus making this process the more energetic of the two.

The appearance potentials of a fragment ion sequence will therefore be greater than that of the parent ion and will depend on the parent and the other species formed in the reaction. It should be noted from Equation 3 that the appearance potential of the positive ion product is the same as the appearance potential of the neutral fragment product. The appearance potential of a given fragment, e.g., CH_3CO^+ , varies from compound to compound, as illustrated in Table 2.⁹

The construction of a mass spectrometer which can detect neutral fragments makes possible another method in which the decomposition of molecules by means of energetic electrons can be studied.¹⁰ If the ion intensity of ionized neutral par-

Table 2. Appearance Potentials of CH_3CO^+

Source	Other Products	Appearance Potential(eV) ⁹
CH_3CO	---	8.05 (Ionization Potential)
CH_3CHO	$\text{H}\cdot$	11.67
$\text{C}_2\text{H}_5\text{OH}$	$\text{H}_2 + \text{H}\cdot$	14.5
CH_3COCH_3	$\text{CH}_3\cdot$	11.16
$\text{CH}_3\text{COC}_2\text{H}_5$	$\text{C}_2\text{H}_5\cdot$	11.40

ticles is plotted against the m/z ratio, a neutral fragment spectrum characteristic of the compound is obtained. If the ion intensity for a particular species is plotted against the energy of the electron beam, holding the m/z ratio constant, an ionization potential plot results. But whereas the appearance potentials are dependent on the origin of the particle and the other fragments formed, this ionization potential should depend only upon the energy needed to remove an electron from the neutral fragment in question, and should thus remain constant for a given neutral fragment from several different compounds, unless they are formed in an excited state. Neutral fragment spectra, or neutral spectra,

can thus be used to study fragmentation patterns and products and to measure the ionization potentials and appearance potentials.

In this work, the neutral fragment mass spectrometer will be used to study the fragmentation patterns of ketones and to determine the ionization potentials of neutral fragments formed from them, the appearance potentials of positive ions, and the enthalpies of formation of positive ions and neutral species.

BRIEF DESCRIPTION OF INSTRUMENT

The instrument has been described previously¹⁰ and was used without modification for these experiments. A brief description is in order. A cylindrical vacuum chamber constructed of 16 gauge stainless steel, 10.5 in. i.d., and 11 in. in height, encloses the ion source and quadrupole mass filter(Electronics Assoc. Inc., Model 51P-224A, Quad 150A, powered by Quadrupole Power Supply, Model QPS, Extranuclear Labs, Inc.).

Fitted atop the mass filter is a deflector, which deflects the ions passing through the mass filter to an offset 17-stage Cu-Be electron multiplier(Balzers High Vacuum Corp., Model Sev-17), powered by a high voltage power supply(Fluke Mfg., Inc., Model 413C). The offset is necessary to prevent a direct optical path between the ion source and the electron multiplier. The signal from the electron multiplier is processed by a preamplifier which separates the pulsed(260 Hz, AC) neutral fragment signal from the DC positive ion signal. The positive ion signal can then be recorded directly.

The AC neutral fragment signal is produced by pulsing the electron beam in the primary chamber, producing neutral fragments in pulses. The method of pulsing will be discussed later. The pulsed signal due to ionization of the neutral

fragments is led from the preamplifier into a phase-sensitive detector(Princeton Applied Research, Model 122), using an externally generated square wave as a reference (Hewlett-Packard, Model 211AR). The AC signal is thus synchronously rectified and amplified and then recorded as the neutral fragment spectrum. Figure 3 shows the general configuration of the mass spectrometer. Figure 4 illustrates the signal processing circuitry.

Details of the ion source are given in Figure 5. The electron beams are opposed 180° . The pulsed grid, 1Y Grid II, is connected to the square wave generator by a cable which is shielded inside and outside the vacuum chamber. Positive ions formed in the primary chamber are drawn out by the 1Y Drawout electrode, maintained at -45 V. Neutral fragments diffuse through the 1Y Focus(kinetic energy) and 2Y Repellor grids, both constructed of 92% transparent tungsten mesh.

Ionization of the neutral fragments(for neutral spectra) or of fresh sample(for normal positive ion mass spectra with no primary chamber processes taking place), then occurs in the secondary chamber. Positive ions are drawn out by the 2Y Drawout and 2Y Focus(kinetic energy) grids, again constructed of 92% transparent tungsten mesh.

The centers of the two chambers are separated by 8 mm

Figure 3. Mass Spectrometer Equipment Configuration¹⁰

SCHEMATIC DIAGRAM OF OUTPUT SIGNAL CIRCUITRY

Figure 4. Signal Processing Circuitry¹⁰

Figure 5. Ion Source Configuration¹⁰

and the 2Y Shield is kept ~ 12 V positive with respect to the 1Y Shield, thus preventing any positive ions formed in the primary chamber from passing into the secondary chamber.

The filament currents are controlled by emission regulators described elsewhere.¹¹ Separate power supplies are used for the voltages applied to primary chamber electrodes and secondary chamber electrodes. A small (190 Gauss) magnet is used to collimate the electron beams.

In order to provide a pressure differential between the sample inlet, located on one side of the ion source and perpendicular to the primary electron beam, and the ion source, a cold finger is mounted opposite the sample inlet. This cold finger is cooled by liquid nitrogen and provides the driving force for a continuous stream of sample gas. A further benefit of the cold finger is that it traps any sample molecules after only one pass through the ion source. Normally, the background pressure in the main vacuum chamber is less than 10^{-7} Torr and samples are run at $3-5 \times 10^{-7}$ Torr.

This pressure is maintained by an ion pump (also used to monitor the pressure, VacIon 921-0011, Varian Associates), an oil diffusion pump (Dow 704 oil) and a Welch 1600 mechanical pump. The diffusion pump is separated from the vacuum chamber by a liquid nitrogen cooled trap.

The inlet system provides for the introduction of gases

and liquids. An expansion chamber provides for the volatilization of the liquids. The resulting gases pass from the expansion chamber through a small orifice in a gold foil into the vacuum chamber. A solid sample inlet source bypassing the gold foil leak is used for compounds of low volatility. The sample chamber is evacuated by an oil diffusion pump (Dow 704 oil) and a Welch 1600 mechanical pump.

Details of the inlet system are given in reference 10.

EXPERIMENTAL

General

Twenty ketones were examined. Sixteen were aliphatic ketones, two were aliphatic diketones and two were aromatic ketones. Table 3 lists the compounds with their vendors. All were checked for purity using a gas chromatograph and none showed obvious impurities. Figure 6 shows the ketones examined; vertical sequences show structural patterns in the compounds selected for this study. Other sequences may also be discerned, e.g., the methyl-n-alkyl ketones and the methyl-iso-alkyl ketones.

Table 3. Ketone Sources

Chem Service, Inc., "Lab Assist": Acetone, acetyl acetone, diacetyl, 2-butanone, 2-pentanone, 3-pentanone, cyclopentanone, cyclohexanone, 2-heptanone, 3-heptanone, 4-heptanone, acetophenone and benzophenone.

Aldrich Chemical: 2-hexanone, 3-hexanone, 5-methyl-2-hexanone, 4,4-dimethyl-2-pentanone and 3-methyl-2-pentanone.

Eastman Kodak Chemicals: 3-methyl-2-butanone.

Fisher Chemicals: 4-methyl-2-pentanone.

Figure 6. Ketones Selected for Analysis

The pressure in the vacuum chamber is measured as a function of current in an ion pump. However, this pressure is ~100 times less than the actual pressure in the ion source due to the location of the sample source and cold surface close to the ion source. The pressure in the ion source is much higher than the overall pressure in the vacuum chamber. Normally, with a few microliters of volatile liquid sample, the indicated pressure is $3-5 \times 10^{-7}$ Torr with a background reading of $< 10^{-7}$ Torr. This would indicate a signal-to-background ratio of about 4 to 1. However, the signal to noise ratio is much greater than this, indicating that the cold surface acts as a pump and creates a pressure differential with respect to background gases. Thus, the cold surface tends to eliminate unwanted background while enhancing the effective concentration of sample in the ion source.

Discrimination Corrections

An electron multiplier was used in series with a preamplifier to amplify the resulting ion currents. Electron multipliers are known to discriminate in their response.¹² In addition, quadrupole mass analyzers also discriminate against ions of increasing m/z . A calibration of this instrument was made previously and was used to correct the mass spectra.¹³

Figure 7. Correction Scale for Mass Discrimination¹⁰

The calibration curve is reproduced in Figure 7. In practice, each measured peak intensity is multiplied by the number necessary to eliminate this discrimination. After extensive use, it became apparent that the mass discrimination was changing with time. For this reason, the mass discrimination factor was not applied to the last ketone studied, diacetyl. In this case, the mass spectrum taken as raw data was used since it was in good agreement with a literature mass spectrum.

The mass spectrum of the neutral fragments is corrected not only for mass discrimination but also for the different ionization cross sections of the neutral fragments diffusing from the primary to the secondary chamber. The larger fragments will have a greater probability for ionization in the secondary chamber than the smaller fragments. The method of Otvos and Stevenson¹⁴ was used to calculate relative cross sections. In essence, this method assigns a relative value for the cross section to each atom and considers any molecular cross section as the sum of the atomic cross sections. Hydrogen is assigned a value of 1.00, carbon is 4.16 and oxygen is 3.29. Thus, the relative ionization cross section for CH_3CO is that for $\text{C}_2\text{H}_3\text{O}$ and equals $2(4.16) + 3(1.00) + 1(3.29) = 14.61$. For these neutral spectra, a correction

factor using the mass discrimination divided by the cross section was used as the total discrimination effect at each m/z . Figure 8 shows the trends of cross section values plotted against molecular weight. Each small series is obtained by adding hydrogen atoms to the beginning fragment of the series.

Following the application of the total discrimination factor, each spectrum is normalized at a constant total ionization. This method compensates for different volatilities of compounds and variations in the instrumental conditions, and allows comparisons to be made more easily.

In order to facilitate comparing the spectra, not all peaks were used in the analyses. The instrument is not able to measure $m/z < 12$ easily, so no attempt was made to analyze species such as H^+ or H_2^+ . Mass 14 was in general not used because of the uncertainty in the discrimination scale (see Figure 7) and its relatively small, constant value from compound to compound. No attempt was made to use any peak measuring less than 1/500 of the base peak of that spectrum.

The mass spectra thus recorded compare well with the known literature spectra, which were normalized in the same manner as the experimental mass spectra. In no case was a literature peak intensity greater than 2% of its base peak excluded from a literature mass spectrum.

Figure 8. Relative Ionization Cross Sections

Analysis Conditions

The temperature in the ion source was measured with a chromel-alumel thermocouple (Baldwin-Lima-Hamilton Corp.) and the normal ion source temperature was $\sim 120^{\circ}\text{C}$. All positive ion mass spectra were taken using electron energies of 50 eV. Literature spectra were not always at 50 eV; some were taken at 70 eV and for some the electron accelerating voltage used was not reported. Neutral fragment spectra were taken using a primary electron beam energy of 50 eV and a secondary beam energy of 11.5, 12.5 and 13.5 eV. Reproduced in this work are the 13.5 eV spectra. Appearance potentials of positive ions were taken using a variable secondary beam energy with no primary chamber processes occurring. Ionization potentials of the neutral fragments were taken using 50 eV primary electron beam energy and a variable secondary electron energy. Table 4 displays the general experimental operating conditions.

Other features of the experimental operating conditions to be noted are: a 12 V shield-to-shield repulsive potential to prevent positive ions formed in the primary chamber from reaching the secondary chamber, and a -45 V drawout electrode in the primary chamber to attract the positive ions that are formed. There is a -50 V drawout

Table 4. Experimental Operating Conditions

Operating Conditions for Obtaining Positive Ion Mass Spectra:

(secondary chamber only)

Trap Current: 30 μ a Shield Voltage: +12 V
Electron Energy: 50 eV Kinetic Energy: -1.7 V
Drawout: - 50 V

Operating Conditions for Obtaining Neutral Fragment Spectra:

Primary Chamber:

Trap Current: 60 μ a Shield Voltage: 0 V
Electron Energy: 50 eV Kinetic Energy: -10 V
Drawout: -45 V

Secondary Chamber:

Trap Current: 30 μ a Shield Voltage: +12 V
Electron Energy: 13.5 eV Kinetic Energy: -1.7 V
Drawout: -50 V

electrode after the secondary chamber to extract positive ions formed there and direct them through the quadrupole mass filter and to the detection system.

The high trap current in the primary chamber is necessary to produce a large number of neutral fragments, which can then diffuse into the secondary chamber. Then a smaller trap current is able to ionize them in the secondary chamber.

In this work, the ionization and appearance potentials are calculated using Warren's method.¹⁵ The ion current is normalized at the same arbitrary intensity as a standard whose ionization or appearance potential is known. The two sets of ion current data are plotted against a linear scale of electron energy, and the difference in energy between the two is extrapolated to zero ion current. The difference from the standard is taken and the resulting potential at zero ion current is referred to as the extrapolated voltage difference (EVD) result.

The appearance potentials and ionization potentials thus taken here have a nominal reading precision of ± 0.05 eV or 1.3 kcal/mole. However, an inspection of the results reveals that too many of the known literature values disagree with these results. Therefore, the claimed precision is possibly the same, but the uncertainty in the accuracy is

better stated as ± 0.10 eV or ± 3 kcal/mole.

Standards

In order to use the EVD method for determining these potentials, it is necessary to have a standard of known appearance or ionization potential, and a known energy scale. The electron energy was determined with a digital voltmeter(Fluke Mfg., Model 8120A) and the data were recorded with an X-Y recorder(Esterline Angus, Model 540T). In this work, the ionization potential(IP) of each pertinent parent molecule(appearance potential of the parent ion) was used as the standard for fragmentation appearance potential(AP) data, except for benzophenone, in which case the parent ion could not be detected. Instead, the base peak, for which a value for the appearance potential is known, was used as the standard. Literature values for the IP of three of the twenty ketones could not be found, viz., 3-hexanone, 1,4-dimethyl-2-pentanone and 5-methyl-2-hexanone. They were determined using this same method, viz., comparison with a known standard, 4-methyl-2-pentanone. The IP of acetone was used as a secondary standard, and indicated an accuracy over a 0.5 eV range to be ± 0.03 eV. The results are given in Table 5.

Table 5. Ionization Potentials

Compound	IP(eV)
4-methyl-2-pentanone	9.31 ⁹
Acetone	9.69 ⁹
Acetone	9.72 (this work)
3-hexanone	9.43 $\pm$ 0.03 (this work)
4,4-dimethyl-2-pentanone	9.03 $\pm$ 0.03 (this work)
5-methyl-2-hexanone	9.39 $\pm$ 0.03 (this work)

An internal standard was available for the neutral fragment ionization potential measurements. Acetylene, mass 26, was used in all cases, except for neutral fragments from 3-heptanone, where ethylene, mass 28, was abundant and was used. Even in this case, acetylene had an ionization potential only 0.02 eV below the accepted value, indicating the reproducibility of the acetylene ionization potential. The value of 11.40 eV for the IP of acetylene is recognized as being the adiabatic IP.¹⁶

DATA

Positive Ion and Neutral Fragment Mass Spectra

Displayed in this section, Figures 9a-t, are the spectra of the twenty selected ketones, corrected for total discrimination effects. Three spectra are shown for each compound. A positive ion mass spectrum from the literature is displayed on the lower part of each page. The experimental positive ion spectrum taken here is shown in the middle of each figure. These two spectra are presented in order to show that the data taken is reliable. While the agreement is not perfect in all cases, in general the literature spectra agree well with the experimental spectra. It has been shown that mass spectra will vary from instrument to instrument, and the present data is no exception.¹⁷ The sources of the literature spectra are listed in Table 6.

The 13.5 eV neutral fragment spectra, corrected for total discrimination, appear at the top of each figure, plotted with increasing m/z , left to right. The positive ion spectra referred to above are plotted in reverse m/z , in order to show the relationship between the fragmentation patterns occurring more clearly. Following these spectra, a neutral fragment spectrum of 2-heptanone, as taken from the instrument, and with no corrections applied, appears in Figure 10 as an example of the data obtained.

Table 6. Literature Mass Spectra

Compound	Reference and Page or Serial No.
Acetone	18, No. 641
Acetyl Acetone	18, No. 806
Diacetyl	18, No. 782
2-butanone	18, No. 644
2-pentanone	18, No. 651
3-pentanone	18, No. 379
3-methyl-2-butanone	18, No. 652
Cyclopentanone	19, p. 123
Cyclohexanone	18, No. 449
2-hexanone	18, No. 661
3-hexanone	18, No. 662
3-methyl-2-pentanone	18, No. 663
4-methyl-2-pentanone	18, No. 380
4,4-dimethyl-2-pentanone	20, p. B2
5-methyl-2-hexanone	19, p. 407
2-heptanone	18, No. 666
3-heptanone	18, No. 667
4-heptanone	19, p. 407
Acetophenone	19, p. 477
Benzophenone	19, p. 1239

Figure 9a. Acetone Spectra

Figure 9b. Acetyl Acetone Spectra

Figure 9c. Diacetyl Spectra

Figure 9d. 2-butanone Spectra.

Figure 9e. 2-pentanone Spectra

Figure 9f. 3-pentanone Spectra

Figure 9g. 3-methyl-2-butanone Spectra

Figure 9h. Cyclopentanone Spectra

Figure 9i. Cyclohexanone Spectra

Figure 9j. 2-hexanone Spectra

Figure 9k. 3-hexanone Spectra

Figure 91. 3-methyl-2-pentanone Spectra

Figure 9m. 4-methyl-2-pentanone Spectra

Figure 9n. 4,4-dimethyl-2-pentanone Spectra

Figure 90. 5-methyl-2-hexanone Spectra

Figure 9p. 2-heptanone Spectra

Figure 9q. 3-heptanone Spectra

Figure 9r. 4-heptanone Spectra

Figure 9s. Acetophenone Spectra

Figure 9t. Benzophenone Spectra

SAMPLE 2-HEPTANONE
 PRESSURE 3x10⁻⁷ DATE 1 DEC 73 OPERATOR O
 RES. SENS: 50mv/in V1 1V/in V2
 SCAN RATE 3000 9 MULTIPLIER 150.0
 PREAMP 10 DEFLECTOR 3.7
 LOCK-IN: SENS 50mv TIME CONST. 3 sec
 FREQUENCY 260 PHASE 3°
 1Y: EAV 50 TRAP 60µa MODE FIL
 SHIELD 0 DO -45 KE -10
 2Y: EAV 13.5 TRAP 30µa MODE TRAP
 SHIELD +12 DO -50 KE -1.7

Figure 10. 2-heptanone Neutral Fragment Spectrum(no corrections applied)

Appearance Potentials

After the positive ion spectrum and neutral fragment spectra of each compound were taken, a series of appearance potentials of the positive ions and the ionization potentials of the neutral fragments were measured. These measurements can be used to characterize the fragments or ions in question. The way in which appearance potential data were treated will be covered in this section. All of the data is listed in Appendix A, in the same order as the spectra appeared in Figure 9 of the previous section.

If an appearance potential study of a particular compound has been previously made and tabulated a check of the literature will suffice to characterize a particular value of appearance potential of given m/z with a particular positive ion. The appearance potentials of the positive ions formed from a particular parent ion may be listed and comparison with experimental values for the same positive ion from the same parent molecule will be easy. For instance, the appearance potential of m/z 85 from 2-hexanone was found experimentally to be 9.75 eV. (See Appendix A.) Reference 9 lists an AP of 9.66 eV for $C_5H_9O^+$ from 2-hexanone. Within ± 0.10 eV, then, m/z 85 from 2-hexanone is characterized as $C_5H_9O^+$.

What neutral products were formed when the parent ion

dissociated to form $C_5H_9O^+$? A mass-balanced equation reads

The heat of the reaction is

$$\begin{aligned}\Delta H_{\text{rxn}} &= \Delta H_f (\text{Products}) - \Delta H_f (\text{Reactants}) \\ &= \Delta H_f (CH_3\cdot) + \Delta H_f (C_5H_9O^+) - \Delta H_f (C_6H_{12}O^+)\end{aligned}$$

Experimentally, this is equal to, $AP(C_5H_9O^+) - AP(C_6H_{12}O^+)$.

From Appendix A, this is $9.75 \text{ eV} - 9.36 \text{ eV} = 0.39 \text{ eV}$ or

$$\begin{aligned}9 \text{ kcal/mole} &= \Delta H_{\text{rxn}} \\ &= \Delta H_f(CH_3\cdot) + \Delta H_f(C_5H_9O^+) - \Delta H_f(C_6H_{12}O^+)\end{aligned}$$

Calculate the heat of formation of $C_5H_9O^+$ by substituting in values for the other unknowns from reference 9: ΔH_f of $CH_3\cdot = +33 \text{ kcal/mole}$ and ΔH_f for $C_6H_{12}O^+ = +149 \text{ kcal/mole}$.

$$9 \text{ kcal/mole} = +33 + \Delta H_f (C_5H_9O^+) - (+149)$$

$\Delta H_f (C_5H_9O^+) = +125 \text{ kcal/mole}$, compared to a literature value of 124 kcal/mole .⁹

In this case, there was little doubt as to the nature of the neutral products formed. In other cases, it may not

be so clear cut, and a number of calculations may be necessary before the correct neutral fragments produced are inferred and the equations balance. An important point is that the AP of the fragment in question need not be previously tabulated. Since the AP will vary from compound to compound, it is not as useful as the heat of formation, which will not vary from compound to compound. Therefore, a cumbersome listing of every AP from every compound is unnecessary. The information can be contained in a listing of the heats of formation.

It is instructive to consider a case which is less clear cut than that of $C_5H_9O^+$ from 2-hexanone.

Diacetyl yields a positive ion of m/z 43 which has an AP of 10.89 eV. Reference 9 lists CH_3CO^+ as having an AP from diacetyl of 9.9 eV with neutral product $CH_3CO\cdot$ being formed in that same reaction. Clearly this is a 1.0 eV difference and some explanation is in order. Suppose that instead of the $CH_3CO\cdot$ neutral radical being formed in that reaction, $CH_3\cdot$ and CO were formed.

$$\begin{aligned}\Delta H_{rxn} &= AP(CH_3CO^+) - AP(CH_3COCOCH_3^+). \text{ From Appendix A,} \\ &= 10.89 \text{ eV} - 9.24 \text{ eV} = 1.65 \text{ eV} = 38 \text{ kcal/mole.}\end{aligned}$$

$$\begin{aligned}38 \text{ kcal/mole} &= \Delta H_f(CH_3\cdot) + \Delta H_f(CO) + \Delta H_f(CH_3CO^+) \\ &\quad - \Delta H_f(CH_3COCOCH_3^+)\end{aligned}$$

Taking values from reference 9 and solving for $\Delta H_f(\text{CH}_3\text{CO}^+)$,

$$38 = 33 + (-26) + \Delta H_f(\text{CH}_3\text{CO}^+) - (+135)$$

$$\Delta H_f(\text{CH}_3\text{CO}^+) = +166 \text{ kcal/mole.}$$

The literature value is + 152 kcal/mole, and this calculation is off by ~14 kcal. Some of this discrepancy may be accounted for by the accumulative effect of uncertainties in the many ancillary values needed for this calculation.

These examples illustrate the technique of inferring neutral products from the energetics of the formation of the complementary positive ions. If the calculations are performed for every positive ion AP of a particular compound, a group of neutral fragments associated with the complementary positive ions will accrue and may be compared with the actual neutral fragment spectrum, depicted in Figure 9 of the previous section.

Notice that in each example of this section, the AP of the positive ion is also the AP of the neutral fragment formed in the same reaction. It may be possible to determine the AP of the neutral fragments directly using the neutral fragment mass spectrometer with some modification (see the Improvements subsection, below). If this becomes possible, such data would confirm or disprove the neutral products inferred from the calculations as presented above.

Since the AP of a given positive ion varies from compound to compound, but the heat of formation does not, the data are presented in Appendix A as experimental values for heats of formation, obtained here and compared to the literature values. Agreement is generally good. All measurements here are subject to the bias introduced by vertical ionization and this may lead to errors, generally $\sim 0.2 \text{ eV}^{21}$ or $\sim 5 \text{ kcal/mole}$ or less. The claimed precision is $\pm 0.10 \text{ eV}$, or 2 kcal/mole , for a total accuracy of $\pm 7 \text{ kcal/mole}$, with most errors expected to be on the high side, i.e., more positive AP's and heats of formation than the accepted values.

Figure 11 shows some appearance potential data as obtained from the instrument for positive ions from 2-heptanone. m/z 59 is $\text{C}_3\text{H}_7\text{O}^+$, m/z 71 is $\text{C}_5\text{H}_{11}^+$ and m/z 72 is $\text{C}_4\text{H}_8\text{O}^+$. Note that m/z 72 has a wide (noisy) trace, indicating that it is not abundant.

Figure 11. 2-heptanone Appearance Potential Data

Ionization Potentials

The ionization potentials of the neutral fragments are arranged according to mass in Appendix B. In general, the ionization potentials listed are indicative of either one or two species. In the case of two species, it seems clear that one must be a hydrocarbon and the other an oxygen-containing compound. Among the interesting masses displaying two possible species are masses 28, 42, 43 and 56. Note that the oxygen-containing species have the higher ionization values.

The ionization potentials are subject to the uncertainty due to vertical ionization previously discussed. The average ionization potential for each species which was reproducible over a number of compounds, or which agreed with a literature value, is presented in Table 7. It is interesting to note that almost all of the small disagreements are on the high side, indicating that the uncertainty due to vertical ionization is at least partly responsible for the differences. Again, the total error is probably ± 0.3 eV for each measurement, ± 0.10 due to the instrument and ± 0.2 eV due to vertical ionization, for a total error of ± 0.3 eV. The bias is expected to be positive.

A few of the values listed in Table 7 as a result of this work need special explanation. Only one value is seriously below its literature value, that for CO, by 0.4 eV, and this may indicate that CO is excited as a result of its

mode of formation from ketones.

The values for three fragments, $C_2H_5\cdot$, $CH_3CO\cdot$ and C_3H_6O , do not agree with accepted literature values. Yet for $C_2H_5\cdot$, a check on the data listed in Appendix B reveals consistent, reproducible results. No simple explanation is apparent. In the case of $CH_3CO\cdot$, the experimental values are not so reproducible, but an enol structure for this fragment would account for a higher ionization potential. However, it should be pointed out that the literature value of 8.05 eV for the IP of $CH_3CO\cdot$ is the result of only one author, with no outside confirmation. In the case of C_3H_6O , three values are within .03 eV of 9.99 eV. This fragment, believed to be the enol structure, has only one listed value and no confirming values. Indeed, a theoretical calculation of the IP of enol- C_3H_6O , also listed in Reference 9, gives a value of 9.97 eV, which is in good agreement with the value of 10.1 eV obtained in this work.

Figure 12 shows some automatically produced ionization potential data of ions from neutral fragments of 2-heptanone. Mass 39 is $C_3H_3\cdot$; mass 40 is C_3H_4 ; and mass 41 is $C_3H_5\cdot$. The internal standard for 2-heptanone was acetylene, mass 26, which has an adiabatic IP of 11.40 eV, as discussed previously.¹⁶

Table 7. Average Ionization Potentials of Neutral Fragments

Formula	Mass	IP(eV)(this work)	Lit. ^a (eV)
CH ₃ ·	15	9.88 ± 0.05	9.84
C ₂ H ₃ ·	27	9.7 ± 0.3	9.4
C ₂ H ₄	28	10.57 ± 0.2	10.45
CO	28	13.6 ± 0.3	14.01
C ₂ H ₅ ·	29	9.34 ± 0.10	8.4
C ₃ H ₃ ·	39	9.5 ± 0.2	---
C ₃ H ₄	40	10.5 ± 0.2	10.36
C ₃ H ₅ ·	41	8.94 ± 0.1	8.15
C ₃ H ₆	42	9.62 ± 0.10	9.73
CH ₂ CO	42	9.94 ± 0.05	9.99 ²²
C ₃ H ₇ ·	43	8.7 ± 0.3	8.1
CH ₃ CO·	43	10.1 ± 0.3	8.05
C ₄ H ₆	54	9.9 ± 0.1	9.6
C ₄ H ₇ ·	55	8.6 ± 0.2	8.0
C ₃ H ₃ O·	55	9.0 ± 0.2	---
iso-C ₄ H ₈	56	9.36 ± 0.05	9.23
C ₃ H ₄ O	56	10.18 ± 0.2	10.14
C ₃ H ₅ O·	57	10.15 ± 0.10	---
C ₃ H ₆ O	58	10.1 ± 0.2	8.93
C ₃ H ₇ O·	59	9.8 ± 0.2	---
C ₃ H ₄ O ₂	72	9.60 ± 0.05	9.60

^aAll literature values taken from Reference 9 unless noted otherwise, and represent adiabatic IP's.

Figure 12. 2-heptanone Ionization Potential Data

RESULTS AND DISCUSSION

Correlation of Spectra

Neutral fragment mass spectra observed during this work resemble positive ion mass spectra in that the recognized patterns of fragmentation in ketones are observed. Stevenson's rule²³ states that when a bond in a positive ion is broken, resulting in another positive ion and a neutral fragment, the charge remains on the fragment of lowest ionization potential. A neutral fragment spectrum should therefore consist of species with higher ionization potentials than a positive ion spectrum. A study of the species characterized by AP measurements of positive ions and IP measurements of neutral fragments tends to uphold this idea. For instance, AP measurements indicate that m/z 42 is the positive ion $C_3H_6^+$, which has an IP of 9.77 eV,⁹ in most of the positive ion spectra. However, IP measurements indicate that the neutral fragment of mass 42 is CH_2CO , which has an IP of 9.99 eV,²² in most of the neutral fragment spectra.

Therefore, even though the positive ion and neutral fragment spectra resemble each other, they are not composed of entirely the same species.

Suppose that all ionization processes in the mass spectrometer began and ended with the parent molecular ion. Then once a positive ion or neutral fragment was formed, it would not dissociate into smaller fragments. If this were true, the positive ion spectrum plotted in reverse would be the same as the neutral fragment spectrum. The reaction

would yield a positive ion and a neutral fragment. But the parent in this example could also undergo other reactions, such as

The positive ion would appear in the positive ion spectrum and the neutral fragments, formed in the same amounts as their complementary positive ions, would appear in the neutral fragment mass spectrum.

Unfortunately, this is not the case, since it is gen-

erally recognized that subsequent fragmentation of these first products is also possible.²⁴ That is, following the above reactions, others may occur:

Attempts were made to correlate the observed neutral fragment spectra and the positive ion spectrum of a given ketone. The theory of mass spectra, especially the quasi-equilibrium theory,²⁵ has not been developed sufficiently to be of much help for such large, polyatomic molecules. Following the previously mentioned corrections for discrimination and normalization, a comparison of the relative intensities of neutral fragments to positive ions did not seem to follow any numerical pattern related to AP, IP, or heat of formation. Therefore, a simplistic approach of calculating the relative abundance of a given neutral fragment to that of the positive ion at a given m/z was adopted. This was done using the 50 eV positive ion spectrum obtained experimentally, and the 11.5, 12.5 and 13.5 eV neutral fragment spectra obtained experimentally. That is, if the intensity of the positive ion of m/z 42 was x, and the

neutral fragment spectra showed a mass 42 peak intensity of a, b, and c, for the three spectra, then the ratios of a/x , b/x and c/x were calculated. The ratio of intensities was found to approach unity as the secondary electron beam energy was increased. However, this was not the case for all m/z values. Over the range of ketones studied, the following m/z values did not approach unity as the electron energy was increased: 26, 27, 28, 29 and 41.

Shown below in Table 8 is a representative worksheet showing ratios of the intensity of a given neutral fragment divided by the intensity of the positive ion of the same m/z for that compound, in this case 5-methyl-2-hexanone. In this case, only the ratios of masses 27, 41 and 58 do not appear to approach unity. The point of the study is that as electron energy is increased, the neutral fragment mass spectra appear to become more and more like the positive ion mass spectra, even though the two types of spectra may be composed of different species.

The neutral fragment spectra may be composed of neutrals formed from disociation of ions formed under electron impact in the primary chamber of the mass spectrometer, which diffuse into the secondary chamber as small particles; and those formed as a result of dissociation of larger, excited molecules which diffused into the sec-

Table 8. Ratio of Neutral Fragment to Positive Ion Intensity

5-methyl-2-hexanone

m/z	11.5 eV	12.5 eV	13.5 eV
15	2.23	2.72	1.86
26	1.65	1.47	1.24
27	.41	.12	.10
28	.54	1.45	1.24
29	0	.29	.25
39	.27	.36	.31
40	1.65	1.47	2.53
41	.30	.27	.23
42	1.85	1.24	1.76
43	.13	.27	.38
55	.81	.29	.37
56	2.16	2.25	1.50
57	1.03	.92	1.44
58	1.82	1.71	1.75
59	4.47	2.07	2.88
71	.94	2.36	1.62
81	1.85	1.24	1.76

ondary chamber. If this latter process did not occur, then the neutral spectra would show little dependence on the secondary electron beam energy. That is, an increase in the secondary electron beam energy will have greater effect on particles of lower ionization potential, such as excited parent molecules formed in the primary beam. A significant amount of such parent molecules in the secondary chamber will produce a spectrum strongly dependent on electron energy. Such spectra would be characterized by significant peaks at high masses, especially the parent.

It is instructive to consider the process by which a parent molecule diffuses from the primary chamber to the secondary chamber. Only those species reacting with the pulsed electron beam in the primary chamber will be detected in this instrument.

Only those neutrals formed in 260 Hz pulses will be detected as a neutral fragment spectrum in this instrument. If a parent molecule in the primary chamber is excited under electron impact, it may ionize immediately, and be drawn off by the 1Y drawout electrode, or it may become excited and then diffuse into the secondary chamber. These excited parent molecules will reach the secondary

chamber in 260 Hz pulses. There, they will be subject to electron impact and the resulting neutral fragment spectra will be dependent on the energy of the secondary electron beam. The parent molecules most susceptible to such behavior will be those with the highest IP, i.e., the greatest probability of being excited without losing an electron.

The ketone of highest IP studied here was acetone, with an IP of 9.69 eV. The ketone of lowest IP was acetyl acetone, which has an IP of 8.87 eV. A ketone of intermediate IP, 3-methyl-2-butanone, had an IP of 9.31 eV. Figures 13, 14 and 15 depict the neutral fragment spectra of these compounds at the three energies used: 11.5, 12.5 and 13.5 eV. The spectra are all plotted with increasing m/z left to right.

It is clear that the changing electron energy affects the acetone the most and acetyl acetone the least, with the expected intermediary results for 3-methyl-2-butanone. This tends to confirm the suspicion that excited parent molecules are indeed formed and do diffuse into the secondary chamber for reaction and detection.

Figure 13. Acetone Neutral Fragment Spectra

Figure 14. Acetyl Acetone Neutral Fragment Spectra

Figure 15. 3-methyl-2-butanone Neutral Fragment Spectra

Disregarding the phenomenon of formation of neutral particles from excited parent molecules in the secondary chamber, it is possible to attempt a correlation of the positive ion mass spectrum with the neutral fragment mass spectrum, assuming that the neutral fragments detected are formed exclusively in the primary chamber. This correlation will involve inspection of the appearance potential data for positive ion fragments and the pertinent neutral fragment products, in order to determine whether the neutral fragment resulting from a large peak in the positive ion mass spectrum does in fact result in a peak of large intensity in the neutral fragment spectrum.

While it is possible to predict generally the large peaks in the neutral fragment spectrum from such a correlation, it is by no means perfect or quantitative. Consider the example of acetone. The largest peak in the positive ion spectrum is m/z 43, CH_3CO^+ . The presumed resulting neutral fragment is $\text{CH}_3\cdot$. Hence it is to be expected that the largest peak in the neutral spectrum is due to $\text{CH}_3\cdot$, namely, m/z 15. But the largest peak in the neutral spectrum is again 43, CH_3CO . This is probably accounted for by the explanation of the reacting excited species in the secondary chamber; the parent molecule favors α -cleavage

and of the two possible modes of reaction, i.e., to CH_3^+ and $\text{CH}_3\text{CO}\cdot$ or to $\text{CH}_3\cdot$ and CH_3CO^+ , the latter is favored by Stevenson's rule, since $\text{CH}_3\cdot$ has the higher ionization potential.

This method of correlation works better for larger molecules, and especially those of lower or intermediate IP. The compound 2-heptanone has an IP of 9.33 eV. Peaks prominent in the positive ion spectrum occur at m/z :

15, 27, 29, 39, 41, 43, 55, 58, 59, 71, 72, 85 and 99.

A check on the appearance potential data of Appendix A reveals that the neutral fragments resulting from the formation of the above positive ion spectrum should include those of mass:

15, 26, 28, 29, 42, 43, 55, 56, 57, 58, 59, 72 and 99.

The neutral fragment spectrum reveals prominent peaks at:

15, 28, 42, 43, 56, 57, 58, 59, 71, 72, 85 and 99.

The unexpected peaks are 71 and 85, probably C_5H_{11} and $\text{C}_4\text{H}_9\text{CO}$, and the same explanation for peaks of high mass that was used for acetone and the same explanation concerning excited parent molecules ionizing in the secondary chamber fits in well here.

Ten of the ketones analyzed here have at least one aliphatic chain of three carbons or more and may undergo the McLafferty rearrangement. In all cases, the McLafferty positive ion is prominent in the positive ion spectrum and the eliminated alkene is prominent in the neutral fragment spectrum. The results of the survey are shown in Table 9.

Table 9. McLafferty Reaction Products

Ketone	Positive Ion Mass	Alkene Elim.
2-pentanone	58	C_2H_4
2-hexanone	58	C_3H_6
3-hexanone	72	C_2H_4
3-methyl-2-pentanone	72	C_2H_4
4-methyl-2-pentanone	58	C_3H_6
4,4-dimethyl-2-pentanone	58	C_4H_8
5-methyl-2-hexanone	58	C_4H_8
2-heptanone	58	C_4H_8
3-heptanone	72	C_3H_6
4-heptanone	58	C_4H_8
4-heptanone	86	C_2H_4

Only one ketone of those studied is expected to be involved in a double McLafferty rearrangement²⁶, viz., 4-heptanone. In this case there is a second McLafferty product of m/z 58, with elimination of C₂H₄ according to this sequence:

However, the appearance potential of m/z 58 seems to favor the formation of an isomer of C₄H₈ (see Appendix A) rather than two molecules of C₂H₄. On the basis of a heat of formation calculation, the ΔH_f of m/z 58 favors the formation of C₄H₈ over 2 molecules of C₂H₄ by about 25 kcal/mole. A cyclic intermediate structure may be involved, since 4-heptanone has no chain of four aliphatic, hydrogenated carbons. To further compound the situation, the appearance potential measurements on the positive ion of m/z 86 from 4-heptanone, also mentioned in the table above, indicate that a keto structure is favored, rather than the expected McLafferty enol structure.²⁷

Further work may be needed to clarify the situation with regard to 4-heptanone, but this study was intended to reinforce the idea that neutral fragments may be inferred from their complementary positive ions, and from calculations of the heats of formation of the species involved.

Somewhat surprising is the appearance in the neutral spectra of rearranged ketones of length smaller than the parent. These products may be the neutral equivalent of a McLafferty product(i.e., an enol structure) or a rearranged ketone. In any case, the appearance potential of the alkene positive ion is consistent with the formation of the neutral products listed below in Table 10. These products are generally prominent in the neutral spectrum of the given compound. Note that only the shortest of all ketones capable of undergoing a McLafferty reaction, 2-pentanone, is excluded.

The apparent formation of a neutral fragment of mass 72 in the spectrum of 4-heptanone is interesting. The appearance potential of the complementary ion, m/z 42 ($C_3H_6^+$) in the positive ion spectrum at a value of 11.67 eV indicates a ΔH_f of -28 kcal/mole for the mass 72 product, C_4H_8O , neutral, which is consistent with the enol structure, $C_2H_5COH=CH_2$. Again, as in the formation of the positive ion of m/z 86 cited in the previous study, a cyclic intermediate

structure of 4-heptanone is implied by the concerted loss of $C_3H_6^+$ and the formation of the enol, which cannot be explained by α -cleavage alone. However, some form of rearrangement across the carbonyl group cannot be ruled out entirely.

One other interesting point in this study is that the loss of $C_3H_6^+$ in the above reactions is always accompanied by the formation of the enol structure, while loss of $C_2H_4^+$ and $C_4H_8^+$ is not accompanied exclusively by formation of keto or enol structures. No ready explanation is offered for this phenomenon.

Finally, the structure of $C_5H_9O^+$ from 2-hexanone and 5-methyl-2-pentanone is known from metastable studies²⁸ to be

The ΔH_f data listed in Appendix A indicate that this structure is formed from the above two compounds, as well as from 4-methyl-2-pentanone, with a ΔH_f of 125 ± 5 kcal/mole, vs. a literature value of 124 kcal/mole.⁹ The $C_5H_9O^+$ from 3-methyl-2-pentanone, 3-hexanone, 4,4-dimethyl-2-pentanone and 3-heptanone has a ΔH_f of 138 ± 3 kcal/mole and evidently has the structure $C_4H_9CO^+$. The $C_5H_9O^+$ ion formed from 2-heptanone has a ΔH_f of 132 kcal/mole and its structure is unknown.

Table 10. Rearranged Ketone Neutral Products

Source	Mass	Formula	Alkene Positive Ion Eliminated
2-hexanone	58	$\text{CH}_3\text{COH}=\text{CH}_2$	C_3H_6^+
2-hexanone	72	$\text{CH}_3\text{COC}_2\text{H}_5$	C_2H_4^+
3-hexanone	72	$\text{CH}_3\text{COC}_2\text{H}_5$	C_2H_4^+
3-methyl-2-pentanone	58	$\text{CH}_3\text{COH}=\text{CH}_2$	C_3H_6^+
3-methyl-2-pentanone	72	$\text{CH}_3\text{COH}=\text{CHCH}_3$	C_2H_4^+
4-methyl-2-pentanone	58	$\text{CH}_3\text{COH}=\text{CH}_2$	C_3H_6^+
4,4-dimethyl-2-pentanone	72	$\text{CH}_3\text{COH}=\text{CHCH}_3$	C_3H_6^+
5-methyl-2-hexanone	86	$\text{CH}_3\text{COC}_3\text{H}_7$	C_2H_4^+
5-methyl-2-hexanone	72	$\text{CH}_3\text{COH}=\text{CHCH}_3$	C_3H_6^+
5-methyl-2-hexanone	58	CH_3COCH_3	C_4H_8^+
2-heptanone	58	CH_3COCH_3	C_4H_8^+
2-heptanone	72	$\text{C}_2\text{H}_5\text{COH}=\text{CH}_2$	C_3H_6^+
3-heptanone	58	CH_3COCH_3	C_4H_8^+
4-heptanone	58	$\text{CH}_3\text{COH}=\text{CH}_2$	C_4H_8^+
4-heptanone	72	$\text{C}_2\text{H}_5\text{COH}=\text{CH}_2$	C_3H_6^+
4-heptanone	86	$\text{C}_3\text{H}_7\text{COH}=\text{CH}_2$	C_2H_4^+

Heats of Formation of Positive Ions

Presented below in Table 11 are the heats of formation of positive ions calculated from their appearance potentials and not reported elsewhere.

Table 11. Heats of Formation of Positive Ions

Formula	Mass	Source	ΔH_f (kcal/mole)
$C_3H_4O^+$	56	5-methyl-2-hexanone 2-heptanone	$+193 \pm 3$
$C_5H_7^+$	67	4-methyl-2-pentanone	$+228 \pm 3$
$C_4H_5O^+$	69	cyclohexanone	$+148 \pm 3$
$iso-C_5H_{11}^+$	71	5-methyl-2-hexanone	$+178 \pm 3$
$C_5H_7O^+$	83	cyclohexanone	$+149 \pm 3$
$C_4H_9CO^+$	85	3-methyl-2-pentanone 3-hexanone 4,4-dimethyl-2-pentanone	$+138 \pm 3$
$C_4H_5O_2^+$	85	acetyl acetone	$+115 \pm 3$
$C_6H_{11}O^+$	99	3-heptanone 4-heptanone 5-methyl-2-hexanone 4,4-dimethyl-2-pentanone	$+141 \pm 3$

Heats of Formation of Neutral Fragments

Presented below in Table 12 are the heats of formation of neutral fragments not previously reported, calculated from the appearance potentials of the complementary positive ions. An example of these calculations is given in Appendix A.

Table 12. Heats of Formation of Neutral Products

Formula	Mass	Source	ΔH_f (kcal/mole)
$\text{CH}_3\text{COCO}\cdot$	71	diacetyl acetyl acetone	-15 ± 3
$\text{CH}_3\text{COCH}_2\text{CO}\cdot$	85	acetyl acetone	-5 ± 3
$\text{C}_3\text{H}_3\text{O}\cdot$	55	cyclopentanone	$+20 \pm 3$
$\text{C}_2\text{H}_5\text{CO}\cdot$	57	3-pentanone 3-hexanone	-9 ± 5
$\text{CH}_3\text{CHOHCH}_2\cdot$	59	2-heptanone 5-methyl-2-hexanone	$+13 \pm 3$
$\text{C}_4\text{H}_5\text{O}\cdot$	69	cyclohexanone	$+34 \pm 3$
$\text{C}_3\text{H}_7\text{CO}\cdot$	71	3-hexanone 4-heptanone	-10 ± 3
$\text{CH}_3\text{COH=CHCH}_3$	72	3-methyl-2-pentanone 5-methyl-2-hexanone 4,4-dimethyl-2-pentanone	-16 ± 3
$\text{C}_2\text{H}_5\text{COH=CH}_2$	72	2-heptanone 4-heptanone	-29 ± 3
$\text{C}_4\text{H}_9\text{CO}\cdot$	85	3-methyl-2-pentanone 2-hexanone 3-heptanone	-1 ± 3
$\text{C}_3\text{H}_7\text{COH=CH}_2$ (?)	86	4-heptanone	-41 ± 5
$\text{C}_5\text{H}_{11}\text{CO}\cdot$	99	2-heptanone	$+28 \pm 3$
iso- $\text{C}_5\text{H}_{11}\text{CO}\cdot$	99	5-methyl-2-hexanone	$+17 \pm 3$

Improvements

One essential change was made to the instrument following these experiments in the hope of extending and improving its capabilities. This is the method of pulsing the primary electron beam. The former method was to apply a square wave pulse via a large capacitor connected to a positive power supply. This acted as a sink for the square wave pulses. When pulsing was initiated, the electron current to the trap was halved, indicating that the square wave acted to apply a more negative potential to 1Y Grid II, thus cutting off the electron beam. This method was efficient, but it was felt that switching times through a large capacitor were possibly inordinately longer than necessary, especially since a rate of 260 Hz was desired.

The new method simply connects a square wave source to the grid through a PNP transistor which acts as an amplifier and a switch. The action of the PNP transistor(2N4889) shown in Figure 16, is to apply a more positive potential to the grid. The amplitude of the square wave is adjusted until the trap current is doubled. This circuit results in much faster switching times and gives a sharper pulse. The end result is that lower electron energies may now be applied in the primary chamber, making possible an experiment to determine directly the appearance potential of

neutral fragments. That is, the primary electron energy can now be scanned at low energy (8-13 eV) and neutral particles formed may diffuse to the secondary chamber. There a 50 eV electron beam would ionize the neutral fragments, and they would then be drawn out, mass filtered and led into the detection system. Thus, the appearance potentials of neutral fragments could be determined directly.

AUTOMATIC SCAN CIRCUIT

Figure 16. Improved 1Y Grid II Pulsing Circuit

SUMMARY

Neutral fragment mass spectra were found to be similar in appearance to positive ion mass spectra and were qualitatively correlated. It was discovered that two processes were responsible for the formation of neutral fragment mass spectra: fragmentation in the primary chamber and ionization of excited parent molecules in the secondary chamber. Different species are at least partly responsible for peaks of the same m/z in the two types of spectra, showing that the two spectra are distinct.

The generally good agreement found for the calculated heats of formation of positive ions with their literature values lends confidence to the calculated heats of formation of other positive ions and neutral fragments attempted here.

The technique of inferring neutral species from the appearance potential of the complementary positive ion was confirmed by a study of the McLafferty rearrangement. The salutary results from this study further reinforced the confidence in calculated heats of formation and in the correlation of the neutral and positive ion spectra. The appearance of ketones and enols shorter than the parent in neutral fragment spectra was noted.

Some questions were raised, however, during this work

and satisfactory answers to the following questions were not given. Does 4-heptanone undergo a double McLafferty rearrangement in a concerted, one-step process with a cyclic intermediate structure? Does 4-heptanone eliminate C_3H_6^+ in the formation of $\text{C}_2\text{H}_5\text{COH}=\text{CH}_2$ by means of a cyclic intermediate structure? Why do ketones able to undergo a McLafferty reaction form only an enol structure upon elimination of C_3H_6^+ ?

BIBLIOGRAPHY

1. H. Budzikiewicz, C. Djerassi and D.H. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, San Francisco, 1967, Chap. 3.
2. J.H. Beynon, R.A. Saunders and A.E. Williams, Mass Spectra of Organic Molecules, Elsevier, Amsterdam, 1968.
3. F.W. McLafferty, Anal. Chem., 31, 82 (1959).
4. E. Murad and M. Inghram, J. Chem. Phys., 40, 3263 (1964).
5. J.H. Beynon, R.A. Saunders and A.E. Williams, Mass Spectra of Organic Molecules, Elsevier, Amsterdam, 1968, p. 197.
6. R.G. Cooks, J.H. Beynon, R.M. Caprioli and G.R. Lester, Metastable Ions, Elsevier, Amsterdam, 1973, p. 169.
7. F.H. Field and J.L. Franklin, Electron Impact Phenomena, Academic Press, New York, 1957, p. 26.
8. H. Ehrhardt, in Advances in Mass Spectrometry, Vol. 5, edited by A. Quayle (Institute for Petroleum, London, 1971) p. 82.
9. J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl and F.H. Field, Ionization Potentials Appearance Potentials and Heats of Formation of Gaseous Positive Ions, National Bureau of Standards, NSRDS-NBS, U.S. Government Printing Office, Washington, D.C., 1969.
10. J.R. Reeher, Ph.D. thesis, Iowa State University (1974) (unpublished).
11. G.R. Sparrow, Ph.D. thesis, Iowa State University (1966) (unpublished).
12. R.C. Lao, R. Sander and R.F. Pottie, Int. J. Mass Spectrom. Ion Phys., 10, 309 (1972).
13. J.R. Reeher, op. cit., p. 64.
14. J. Otvos and D. Stevenson, J. Amer. Chem. Soc., 78, 546 (1956).
15. J.W. Warren, Nature, 165, 810 (1950).

16. A.J.C. Nicholson, J. Chem. Phys., 43, 1171 (1965).
17. H. Budzikiewicz, C. Djerassi and D.H. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, San Francisco, 1967, p. 9.
18. Catalogue of Mass Spectral Data, American Petroleum Institute, Research Project 44, Texas A and M University, College Station, Texas.
19. Atlas of Mass Spectral Data, edited by E. Stenhagen, S. Abrahamsson and F.W. McLafferty, Interscience Pub., New York, 1969.
20. 2nd Supplement to Compilation of Mass Spectral Data, A. Cornu and R. Massot, Heyden and Sons, Ltd., London, 1971.
21. F.H. Field and J.L. Franklin, Electron Impact Phenomena, Academic Press, New York, 1957, p. 81.
22. J. Collin and R. Locht, Int. J. Mass Spectrom. Ion Phys., 3, 465 (1970).
23. D.P. Stevenson, Discussions Faraday Soc., 10, 35 (1971).
24. G. Eadon, C. Djerassi, J.H. Beynon and R.M. Caprioli, Org. Mass Spectrom., 5, 917 (1971).
25. MTP International Review of Science, Physical Chemistry, Vol. 5, Mass Spectrometry, edited by A. Maccoll, Butterworths, London, 1972, Chap. 1.
26. G. Eadon, J. Diekman and C. Djerassi, J. Amer. Chem. Soc., 91, 3986 (1969).
27. J.H. Beynon, R.M. Caprioli and J.W. Shannon, Org. Mass Spectrom., 5, 967 (1971).
28. F.W. McLafferty, D.J. McAdoo and J.S. Smith, J. Amer. Chem. Soc., 91, 5400 (1969).
29. F.P. Lossing, Can. J. Chem., 49, 357 (1971).
30. D. Harrop, A.J. Head and G.B. Lewis, J. Chem. Thermo., 2, 203 (1970).

31. J. DuBois and H. Herzog, J. Chem. Soc., Chem. Comm., 16, 932 (1972).
32. B.J. Cocksey, J.H.P. Eland and C.J. Danby, J. Chem. Soc. B, 7, 790 (1971).

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APPENDIX A

Appearance Potentials and Heats of Formation

Presented in this appendix are the appearance potentials obtained for the positive ions formed from the ketones listed previously in Table 3. The data is presented in the format of Reference 9. The mass of the positive ion of a given formula is presented, followed by the experimental appearance potential of that positive ion.

Using the method explained in the DATA section, the neutral fragments produced in the same reaction with the positive ion are listed. The experimental heat of formation of the positive ion is listed and compared with a literature value. The data are arranged by ketone of origin and the ketones appear in the same order as the spectra which appeared in the DATA section.

The literature values for heats of formation are taken from Reference 9 unless otherwise noted. Two recent values for heats of formation of positive ions are used instead of those preferred in Reference 9. These values agree with more of the other values listed in that reference.

$$\Delta H_f (C_2H_3^+) = +266 \text{ kcal/mole}$$

$$\Delta H_f (C_2H_5^+) = +226 \text{ kcal/mole}^{29}$$

The values used for the ionization potentials of the parent ions are also taken from Reference 9, unless noted otherwise.

A brief explanation of the footnotes for this appendix is in order. Using the method explained in the DATA section, it is possible to calculate the heat of formation of a neutral fragment if the heat of reaction is known, and if the heats of formation of the positive ions which serve as reactants and products are known.

As an example, the AP of m/z 15 from diacetyl is 14.10 eV. The IP of the parent diacetyl molecule (AP of the parent ion) is 9.24 eV. This implies that the heat of the reaction

is $14.10 - 9.24 = 4.86$ eV = +113 kcal/mole. Then,

$$113 \text{ kcal/mole} = \Delta H_f(\text{Products}) - \Delta H_f(\text{Reactants})$$

$$113 = \Delta H_f(\text{CH}_3^+) + \Delta H_f(\text{CH}_3\text{COCO}\cdot) - \Delta H_f(\text{CH}_3\text{COCOCH}_3^+)$$

Obtaining the values for the heat of formation of CH_3^+ and $\text{CH}_3\text{COCOCH}_3^+$ from Reference 9, and substituting,

$$113 \text{ kcal/mole} = 260 + \Delta H_f(\text{CH}_3\text{COCO}\cdot) - (+135)$$

$$113 \quad \quad \quad - 125 + \Delta H_f(\text{CH}_3\text{COCO}\cdot)$$

$$\Delta H_f(\text{CH}_3\text{COCO}\cdot) = -12 \text{ kcal/mole.}$$

ACETONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.16	$\text{CH}_3 + \text{CO} ?$	267	260
26	C_2H_2^+	15.61	$\text{CH}_2\text{O} + \text{H}_2 ?$	335	317
27	C_2H_3^+	15.19	$\text{CO} + \text{H}_2 + \text{H}$	272	266
28	C_2H_4^+	12.75	$\text{CO} + \text{H}_2$	267	253
29	C_2H_5^+	13.39	$\text{CO} + \text{H}$	230	226
39	C_3H_3^+	13.81	$\text{H}_2 + \text{OH}$	257	255
42	CH_2CO^+	10.32	CH_4	203	205
43	CH_3CO^+	10.59	CH_3	159	152
58	$\text{CH}_3\text{COCH}_3^+$	9.69	---	---	171

DIACETYL

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.10	CH_3COCO	--- ^a	260
43	CH_3CO^+	10.89	$\text{CH}_3 + \text{CO}$	166	152
86	$\text{CH}_3\text{COCOCH}_3^+$	9.24	---	---	135

^a Implies $\Delta H_f(\text{CH}_3\text{COCO}) = -12$ kcal/mole.

ACETYL ACETONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.57	$\text{CH}_3\text{COCH}_2\text{CO}$	--- ^a	260
27	C_2H_3^+	15.65	?		266
28	C_2H_4^+	14.10	?		253
29	C_2H_5^+	12.61	CH_3COCO	--- ^a	226
30	C_2H_6^+	10.6	?		
31	CH_3O^+	11.50	?		
32	CH_4O^+	11.69	?		
39	C_3H_3^+	13.3	?		
41	C_3H_5^+	13.75	?		
42	CH_2CO^+	12.72	?		
43	CH_3CO^+	11.37	$\text{CH}_3 + \text{CH}_2\text{CO}$	162	152
53	C_3HO^+	14.11	?		
55	$\text{C}_3\text{H}_3\text{O}^+$	12.25	$\text{C}_2\text{H}_5\text{O}$?	208	190
56	$\text{C}_3\text{H}_4\text{O}^+$	11.66	CH_3CHO ?	226	210
57	$\text{CH}_3\text{COCH}_2^+$	11.47	CH_3CO	--- ^a	---
58	$\text{CH}_3\text{COH}=\text{CH}_2^+$	10.97	CH_2CO	185	178
69	C_3HO_2^+	11.67	?		
71	$\text{C}_3\text{H}_3\text{O}_2^+$	11.38	C_2H_5	155	---
72	$\text{CH}_3\text{COCHO}^+$	10.56	C_2H_4	148	155
85	$\text{CH}_3\text{COCH}_2\text{CO}^+$	9.98	CH_3	115	---
86	$\text{CH}_3\text{COCOCH}_3^+$	9.66	$1/2\text{-C}_2\text{H}_4$?	141	135
100	$\text{CH}_3\text{COCH}_2\text{COCH}_3^+$	8.87	---	---	122

^aImplies $\Delta H_f(\text{CH}_3\text{COCH}_2\text{CO}) = -5$ kcal/mole.

Implies $\Delta H_f(\text{CH}_3\text{COCO}) = -18$ kcal/mole.

Implies $\Delta H_f(\text{CH}_3\text{COCH}_2^+) = +190$ kcal /mole.

2-BUTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.40	?		260
26	C_2H_2^+	15.0	$\text{CH}_2\text{O} + \text{CH}_4$?	331	317
27	C_2H_3^+	14.68	$\text{CH}_2\text{O} + \text{CH}_3$	275	266
28	C_2H_4^+	12.74	$\text{CH}_2\text{CO} + \text{H}_2$	250	253
29	C_2H_5^+	12.44	CH_3CO	233	226
42	C_3H_6^+	11.81	$\text{CH}_2 + \text{CO}$	238	229
43	CH_3CO^+	11.37	C_2H_5 ?	189	152
57	$\text{C}_3\text{H}_5\text{O}^+$	10.44	CH_3	149	143
72	$\text{C}_4\text{H}_8\text{O}^+$	9.52	---	---	161

2-PENTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	15.2	?		
28	C_2H_4^+	13.78	?		
29	C_2H_5^+	14.76	?		
39	C_3H_3^+	18.1	$\text{CH}_3\text{CO} + \text{H}_2 + 2\text{H} \cdot$?	254	255
41	C_3H_5^+	13.8	$\text{CO} + \text{CH}_4 + \text{H} \cdot$?	206	216
42	C_3H_6^+	12.02	$\text{CH}_2\text{CO} + \text{H}_2$	229	229
43	C_3H_7^+	11.4	CH_3CO	205	209
58	$\text{C}_3\text{H}_6\text{O}^+$	10.09	C_2H_4	158	178 ^a
71	$\text{C}_4\text{H}_7\text{O}^+$	10.31	CH_3	141	136
86	$\text{C}_5\text{H}_{10}\text{O}^+$	9.38	---	---	154

^aAlso reported as 158. See Ref. 4,9.

3-PENTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	16.44	?		
27	C_2H_3^+	15.09	$\text{CH}_3\text{O} + \text{C}_2\text{H}_4$?	274	266
28	C_2H_4^+	12.97	$\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2$	250	253
29	C_2H_5^+	11.80	$\text{C}_2\text{H}_5\text{CO}$	--- ^a	226
41	C_3H_5^+	13.8	$\text{CH}_3\text{CO} + \text{H}$?	210	216
42	?	15.82	?		
43	?	12.69	Probably CH_3CO^+ and C_3H_7^+		
57	$\text{C}_3\text{H}_5\text{O}^+$	10.51	C_2H_5	155	143
86	$\text{C}_5\text{H}_{10}^+$	9.32	---	---	153

^aImplies $\Delta H_f(\text{C}_2\text{H}_5\text{CO}\cdot) = -14$ kcal/mole.

3-METHYL-2-BUTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.7	?		
27	C_2H_3^+	14.14	$\text{CO} + \text{C}_2\text{H}_5 + \text{H}_2$	263	266
28	C_2H_4^+	13.6	$\text{CO} + \text{C}_2\text{H}_4 + \text{H}_2$	263	253
29	C_2H_5^+	12.98	CH_3COCH_2	243	226
40	C_3H_4^+	14.17	$\text{CH}_2\text{CO} + 2 \text{H}_2$	278	280
41	C_3H_5^+	12.78	$\text{CH}_3\text{CHO} + \text{H}$	219	216
42	C_3H_6^+	11.92	$\text{CH}_2\text{CO} + \text{H}_2$	226	229
43	$\text{iso-C}_3\text{H}_7^+$	10.97	CH_3CO	184	190
57	$\text{C}_3\text{H}_5\text{O}^+$	11.51	$\text{C}_2\text{H}_4 + \text{H}$	138	143
71	$\text{C}_4\text{H}_7\text{O}^+$	10.01	CH_3	134	136
86	$\text{C}_5\text{H}_{10}\text{O}^+$	9.31	---	---	151

CYCLOPENTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.7	?		
26	C_2H_2^+	14.8	$\text{CH}_3\text{COHCH}_2$? (ethylene oxide)	318	317
27	C_2H_3^+	13.82	?		
28	C_2H_4^+	12.74	CH_2CHCHO	270	253
29	C_2H_5^+	12.70	$\text{CH}_2=\text{CHCO}$	--- ^a	226
39	C_3H_3^+	13.24	?		
40	C_3H_4^+	12.00	?		
41	C_3H_5^+	12.19	?		
42	C_3H_6^+	11.86	CH_2CO	241	229
43	CH_3CO^+	11.19	C_3H_5	153	152
53	C_3HO^+	13.61	$\text{C}_2\text{H}_6 + \text{H}$	235	231
55	$\text{C}_3\text{H}_3\text{O}^+$	11.16	C_2H_5	186	190
56	$\text{iso-C}_4\text{H}_8^+$	10.49	CO	221	221
84	$\text{C}_5\text{H}_8\text{O}^+$	9.26	---	---	167

^aImplies $\Delta H_f(\text{CH}_2=\text{CHCO}) = +20$ kcal/mole.

CYCLOHEXANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	13.8	?		
27	C_2H_3^+	13.74	?		
28	C_2H_4^+	12.59	$\text{CH}_3\text{COCHCH}_2$?	263	253
29	C_2H_5^+	13.18	$\text{C}_4\text{H}_5\text{O}$	--- ^a	226
39	C_3H_3^+	13.05	?		
40	C_3H_4^+	12.87	?		
41	C_3H_5^+	12.16	?		
42	C_3H_6^+	11.25	$\text{CH}_2=\text{CHCHO}$	229	229
43	CH_3CO^+	10.66	?		
53	C_3HO^+	10.58	?		
54	C_4H_6^+	9.87	$\text{CH}_4 + \text{CO}$?	218	236
55	$\text{C}_3\text{H}_3\text{O}^+$	11.53	$n\text{-C}_3\text{H}_7$	190	190
56	$2\text{-C}_4\text{H}_8^+$	10.83	CH_2CO	211	209
57	$\text{C}_3\text{H}_5\text{O}^+$	10.95	$\text{CH}_3\text{C}=\text{CH}_2$	142	143
69	$\text{C}_4\text{H}_5\text{O}^+$	10.71	C_2H_5	148	---
70	$\text{C}_4\text{H}_6\text{O}^+$	10.77	C_2H_4	183	195
71	$\text{C}_4\text{H}_7\text{O}^+$	10.44	C_2H_3	127	136
80	$\text{cyclo-C}_6\text{H}_8^+$	10.14	H_2O	248	218
83	$\text{C}_5\text{H}_7\text{O}^+$	10.24	CH_3	149	---
98	$\text{C}_6\text{H}_{10}\text{O}^+$	9.14	---	---	157

^a Implies $\Delta H_f(\text{C}_4\text{H}_5\text{O}) = + 34$ kcal/mole.

2-HEXANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.2	$\text{n-C}_4\text{H}_9\text{CO}$	--- ^a	260
27	C_2H_3^+	14.84	?		
28	C_2H_4^+	11.6	$\text{CH}_3\text{COC}_2\text{H}_5$	258	253
29	C_2H_5^+	13.77	?		
39	C_3H_3^+	14.0	?		
41	C_3H_5^+	13.33	?		
42	C_3H_6^+	12.34	$\text{CH}_3\text{COH}=\text{CH}_2$	246	229
43	CH_3CO^+	11.33	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$	156	152
56	$\text{iso-C}_4\text{H}_8^+$	11.66	$\text{CH}_2\text{CO} + \text{H}_2$	207	209
57	$\text{n-C}_4\text{H}_9^+$	12.06	CH_3CO	216	218
58	$\text{CH}_3\text{COH}=\text{CH}_2^+$	10.96	C_3H_6	181	178
71	$\text{C}_4\text{H}_7\text{O}^+$	10.50	C_2H_5	150	136
85	$\text{C}_5\text{H}_9\text{O}^+$	9.75	CH_3	125	124
100	$\text{C}_6\text{H}_{12}\text{O}^+$	9.36	---	---	149

^a Implies $\Delta H_f(\text{n-C}_4\text{H}_9\text{CO}) = -1 \text{ kcal/mole}$.

3-HEXANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
27	$C_2H_3^+$	13.94	?		
28	$C_2H_4^+$	10.95	$C_2H_5COCH_3$	245	253
29	$C_2H_5^+$	12.44	C_3H_7CO	--- ^a	226
39	$C_3H_3^+$	13.3	?		
41	$C_3H_5^+$	12.38			
42	CH_2CO^+	11.61	$C_2H_6 + C_2H_4$	209	205
43	$n-C_3H_7^+$	11.78	C_2H_5CO	--- ^a	209
55	$n-C_4H_7^+$	11.38	$CH_3CO + H_2$	201	203
57	$C_2H_5CO^+$	10.83	$CH_3 + C_2H_4$	137	143
58	$CH_3COH=CH_2^+$	10.32	C_3H_6	167	171
71	$C_3H_7CO^+$	9.47	C_2H_5	127	136
72	$^{13}C^{12}C_2H_7CO$	9.47	C_2H_5 (isotopic peak)		
85	$C_5H_9O^+$	10.41	CH_3	141	124
100	$C_6H_{12}O^+$	9.43	---	---	151 ³⁰

^a Implies $\Delta H_f(C_3H_7CO) = -8$ kcal/mole.
 Implies $\Delta H_f(C_2H_5CO) = -4$ kcal/mole.

3-METHYL-2-PENTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	14.13	iso-C ₄ H ₉ CO	--- ^a	260
27	C_2H_3^+	14.65	?		
28	C_2H_4^+	13.29	CH ₃ COH=CHCH ₃	--- ^a	253
29	C_2H_5^+	13.17	?		
39	C_3H_3^+	14.87	?		
40	C_3H_4^+	12.66	?		
41	C_3H_5^+	12.46	?		
42	C_3H_6^+	11.71	CH ₃ COH=CH ₂	220	229
43	CH_3CO^+	11.33	C ₂ H ₅ + C ₂ H ₄	156	152
55	n-C ₄ H ₇ ⁺	11.63	C ₂ H ₅ O	208	203
56	2-C ₄ H ₈ ⁺	11.10	CH ₂ CO + H ₂	203	209
57	s-C ₄ H ₉ ⁺	11.34	CH ₃ CO	200	192
58	$\text{CH}_3\text{COH=CH}_2^+$	11.20	C ₃ H ₆	186	178
71	$\text{C}_4\text{H}_7\text{O}^+$	10.87	C ₂ H ₅	156	136
72	$\text{C}_4\text{H}_8\text{O}^+$	9.54	C ₂ H ₄	164	170
85	$\text{C}_5\text{H}_9\text{O}^+$	10.29	CH ₃	137	124
100	$\text{C}_6\text{H}_{12}\text{O}^+$	9.30 (this work)		---	147 ³¹

^a Implies $\Delta H_f(\text{iso-C}_4\text{H}_9\text{CO}) = -2$ kcal/mole.

Implies $\Delta H_f(\text{CH}_3\text{COHCHCH}_3) = -14$ kcal/mole.

4-METHYL-2-PENTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
27	$C_2H_3^+$	13.99	?		
28	$C_2H_4^+$	13.63	?		
29	$C_2H_5^+$	11.53	$CH_3COH=CHCH_2$	--- ^a	226
40	$C_3H_4^+$	12.86	?		
41	$C_3H_5^+$	12.69	?		
42	$C_3H_6^+$	11.91	$CH_3COH=CH_2$	235	229
43	$iso-C_3H_7^+$	11.80	$CH_2CO + CH_3$	187	190
56	$iso-C_4H_8^+$	11.21	$CH_2CO + H_2$	206	209
57	$iso-C_4H_9^+$	11.73	CH_3CO	208	205
58	$CH_3COH=CH_2^+$	10.66	C_3H_6	180	178
59	$C_3H_7O^+$	10.22	C_3H_4 ?	128	---
67	$C_5H_7^+$	11.72	$CH_3 + H_2O$	228	---
70	$C_4H_6O^+$	10.51	C_2H_6	195	194
71	$C_4H_7O^+$	10.07	C_2H_5	140	136
85	$C_5H_9O^+$	9.56	CH_3	120	124
100	$C_6H_{12}O^+$	9.30	---	---	147 ³¹

^a Implies $\Delta H_f(CH_3COH=CHCH_2) = -25$ kcal/mole.

4,4-DIMETHYL-2-PENTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
27	$C_2H_3^+$	16.2	?		
28	$C_2H_4^+$	14.0	?		
29	$C_2H_5^+$	14.12	?		
39	$C_3H_3^+$	13.76	?		
40	$C_3H_4^+$	14.2	?		
41	$C_3H_5^+$	12.38	?		
42	$C_3H_6^+$	12.03	$CH_3COH=CHCH_3$	--- ^a	229
43	CH_3CO^+	10.33	$C_2H_5 + C_3H_6$	165	152
55	$C_4H_7^+$	9.63	?		
56	$iso-C_4H_8^+$	10.77	$CH_3CO + CH_3$	209	209
57	$n-C_4H_9^+$	11.06	CH_3COCH_2	219	218
58	$CH_3COH=CH_2^+$	10.36	C_4H_8	188	178
59	$C_3H_7O^+$	9.72	C_4H_7 ?	160	---
70	$C_4H_6O^+$	9.77	C_3H_8 ?	217	194
71	$neo-C_5H_{11}^+$	10.36	CH_3CO	200	196
72	$C_4H_8O^+$	9.58	C_3H_6	173	161
83	$cyclo-C_6H_{11}^+$	10.17	CH_3O	192	185
85	$C_5H_9O^+$	9.34	C_2H_5	137	124
86	$C_5H_{10}O^+$	9.30	C_2H_4	158	154
99	$C_6H_{11}O^+$	10.36	CH_3	144	---
114	$C_7H_{14}O^+$	9.03(this work)		---	141 ³¹

^aImplies $\Delta H_f(CH_3COH=CHCH_3) = -19$ kcal/mole.

5-METHYL-2-HEXANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	15.22	iso- $\text{C}_5\text{H}_{11}\text{CO}$	--- ^a	260
27	C_2H_3^+	15.02	$\text{CO} + \text{H}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$	262	266
28	C_2H_4^+	11.03	$\text{CH}_3\text{COC}_3\text{H}_7$	244	253
29	C_2H_5^+	13.37	?		
39	C_3H_3^+	15.99	$\text{CH}_3\text{CO} + \text{C}_2\text{H}_2 + 3 \text{H}_2$	245	255
41	C_3H_5^+	12.84	$\text{CH}_3\text{CO} + \text{C}_2\text{H}_4 + \text{H}_2$	216	216
42	C_3H_6^+	12.48	$\text{CH}_3\text{COH}=\text{CHCH}_3$	--- ^a	229
43	CH_3CO^+	11.37	$\text{C}_3\text{H}_7 + \text{C}_2\text{H}_4$	144	152
55	n- C_4H_7^+	12.79	$\text{C}_3\text{H}_7\text{O}$	--- ^a	203
56	iso- C_4H_8^+	10.65	CH_3COCH_3	224	221
57	$\text{C}_3\text{H}_5\text{O}^+$	10.57	$\text{CH}_4 + \text{C}_3\text{H}_5$	148	143
58	$\text{CH}_3\text{COH}=\text{CH}_2^+$	10.13	C_4H_8	163	178
58	$\text{C}_4\text{H}_{10}^+$	16.42	$\text{C}_3\text{H}_3 + \text{OH}?$	220	215
59	$\text{C}_3\text{H}_7\text{O}^+$	9.51	C_4H_7	125	---
71	$\text{C}_5\text{H}_{11}^+$	11.11	CH_3CO	178 ^b	---
72	$\text{C}_4\text{H}_8\text{O}^+$	10.66	C_3H_6	167	161
85	$\text{C}_5\text{H}_9\text{O}^+$	9.85	C_2H_5	129	124
86	$\text{C}_5\text{H}_{10}\text{O}^+$	9.53	C_2H_4	158	154
99	$\text{C}_6\text{H}_{11}\text{O}^+$	10.68	CH_3	140	---
114	$\text{C}_7\text{H}_{14}\text{O}^+$	9.39 (this work)		---	143 ^c

^aImplies $\Delta H_f(\text{iso-}\text{C}_5\text{H}_{11}\text{CO}) = +17$ kcal/mole.

Implies $\Delta H_f(\text{CH}_3\text{COH}=\text{CHCH}_3) = -15$ kcal/mole.

Implies $\Delta H_f(\text{C}_3\text{H}_7\text{O}) = +13$ kcal/mole.

^bStructure is $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2^+$.

^c ΔH_f of the parent ion is assumed to be -73 kcal/mole.

2-HEPTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
15	CH_3^+	15.8	$\text{n-C}_5\text{H}_{11}\text{CO}$	--- ^a	260
27	C_2H_3^+	15.34	$\text{CO} + \text{H}_2 + \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$	270	266
28	C_2H_4^+	12.4	$\text{CO} + \text{C}_4\text{H}_{10} ?$	270	253
29	C_2H_5^+	13.39	$\text{CO} + \text{C}_4\text{H}_9 ?$	243	226
39	C_3H_3^+	16.2	$\text{CH}_3\text{CO} + 3 \text{H}_2 + \text{C}_2\text{H}_2$	252	255
41	C_3H_5^+	13.33	$\text{CH}_3\text{CO} + \text{H}_2 + \text{C}_2\text{H}_4$	214	216
42	C_3H_6^+	11.96	$\text{C}_2\text{H}_5\text{COH}=\text{CH}_2$	--- ^a	229
43	CH_3CO^+	11.13	$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_6$	149	152
55	$\text{n-C}_4\text{H}_7^+$	12.50	$\text{CH}_3\text{CHOHCH}_2$	--- ^a	203
56	$2\text{-C}_4\text{H}_8^+$	10.14	CH_3COCH_3	214	209
57	$\text{n-C}_4\text{H}_9^+$	11.69	CH_3COCH_2	205	218
58	$\text{CH}_3\text{COH}=\text{CH}_2^+$	10.78	C_4H_8	178	178
59	$\text{C}_3\text{H}_7\text{O}^+$	10.31	$\text{C}_4\text{H}_7 ?$	186	---
71	$\text{n-C}_5\text{H}_{11}^+$	11.15	CH_3CO	166	171
72	$\text{C}_4\text{H}_8\text{O}^+$	9.75	C_3H_6	158	161
85	$\text{C}_5\text{H}_9\text{O}^+$	9.84	C_2H_5	132	124
99	$\text{C}_6\text{H}_{11}\text{O}^+$	10.65	CH_3	140	---
114	$\text{C}_7\text{H}_{14}\text{O}^+$	9.33	---	---	143

^a Implies $\Delta H_f(\text{CH}_3\text{CHOHCH}_2) = +13$ kcal/mole.

Implies $\Delta H_f(\text{n-C}_5\text{H}_{11}\text{CO}) = +28$ kcal/mole.

Implies $\Delta H_f(\text{C}_2\text{H}_5\text{COH}=\text{CH}_2) = -26$ kcal/mole.

3-HEPTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
27	$C_2H_3^+$	15.29	?		
28	$C_2H_4^+$	11.39	CO + C_4H_{10}	251	253
29	$C_2H_5^+$	12.82	C_4H_9CO	--- ^a	226
39	$C_3H_3^+$	16.7	$CH_3CO + C_2H_2 + 3 H_2$	265	255
41	$C_3H_5^+$	12.63	$CH_3CO + C_2H_4 + H_2$	215	216
43	$C_3H_7^+$	11.63	?		
55	$n-C_4H_7^+$	11.78	C_3H_7O ?	191	203
56	$2-C_4H_8^+$	10.99	CH_3COCH_3	202	209
57	$C_2H_5CO^+$	11.37	$C_2H_6 + CH_3$	156	143
71	$C_2H_5COCH_2^+$	10.93	$C_3H_6 + H$	127	136
72	$C_2H_5COH=CH_2^+$	10.29	C_3H_6	164	170
85	$C_5H_9O^+$	10.67	C_2H_5 ?	154	124
99	$C_6H_{11}O^+$	10.55	CH_3	142	---
114	$C_7H_{14}O^+$	9.15 ³²	---	---	143

^aImplies $\Delta H_f(C_4H_9CO) = +1$ kcal/mole.

4-HEPTANONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
27	$C_2H_3^+$	14.6	?		
28	$C_2H_4^+$	12.34	$C_3H_7COH=CH_2$?	--- ^a	253
29	$C_2H_5^+$	12.66	$C_4H_9 + CO$	237	226
41	$C_3H_5^+$	13.18	$CH_3CO + C_2H_4 + H_2$	224	216
42	$C_3H_6^+$	11.67	$C_2H_5COH=CH_2$	--- ^a	229
43	$n-C_3H_7^+$	11.67	CH_3CO	--- ^a	209
55	$O_3H_3O^+$	12.12	?		
57	$C_3H_5O^+$	11.20	$C_2H_4 + C_2H_3 + H_2$	139	143
58	$CH_3COH=CH_2^+$	10.93	C_4H_8	182	178
71	$C_3H_7CO^+$	10.63	$C_2H_4 + CH_3$	128	136
72	$^{13}C^{12}C_2H_7CO$	10.61	isotopic peak		
86	$C_3H_7COCH_3^+$	9.87	C_2H_4	144	154
99	$C_6H_{11}O^+$	11.43	CH_3	159	---
114	$C_7H_{14}O^+$	9.15	³² ---	---	139 ³⁰

^a Implies $\Delta H_f(C_3H_7COH=CH_2) = -41$ kcal/mole.

Implies $\Delta H_f(C_2H_5COH=CH_2) = -32$ kcal/mole.

Implies $\Delta H_f(C_3H_7CO) = -12$ kcal/mole.

ACETOPHENONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
17	OH^+	16.5	?		
18	H_2O^+	11.62	?		
27	C_2H_3^+	17.7	?		
28	C_2H_4^+	12.76	?		
39	C_3H_3^+	16.0	$\text{CH}_2\text{CO} + \text{C}_3\text{H}_3$?	271	255
43	CH_3CO^+	11.30	C_6H_5	156	152
51	C_4H_3^+	16.32	$\text{CH}_2\text{CO} + \text{C}_2\text{H}_3$	298	307
52	C_4H_4^+	15.93	$\text{C}_2\text{H}_2 + \text{CH}_2\text{CO}$	302	294
77	C_6H_5^+	12.45	$\text{CH}_3 + \text{CO}$	289	285
78	C_6H_6^+	11.83	CH_2CO ?	265	233
105	$\text{C}_7\text{H}_5\text{O}^+$	9.98	CH_3	174	186
120	$\text{C}_8\text{H}_8\text{O}^+$	9.27	---	---	191

BENZOPHENONE

Mass	Formula	AP(eV)	Other Products	ΔH_f (kcal/mole)	
				Exp.	Lit.
39	$C_3H_3^+$	17.87	?		
50	$C_4H_2^+$	18.26	?		
51	$C_4H_3^+$	18.80	?		
52	$C_4H_4^+$	17.12	?		
53	$C_4H_5^+$	17.23	?		
63	$C_5H_3^+$	16.78	?		
77	$C_6H_5^+$	15.73	?		
78	$C_6H_6^+$	15.99	Benzyne + CO	229	233
105	$C_7H_5O^+$	12.00	C_6H_5	---	217
182	$C_{13}H_{10}O^+$	9.5	(not observed)	---	229

APPENDIX B

Ionization Potentials

The ionization potentials of all neutral fragments from the ketones analyzed are reported here. Since the IP of any neutral fragment should be independent of source, the data are presented in a manner to facilitate comparison and evaluate reproducibility. The uncertainty in each individual measurement is nominally ± 0.05 eV unless otherwise noted.

MASS 15

 $\text{CH}_3^\bullet$

Source	IP(eV)
Acetone	9.86
Acetyl Acetone	9.84
2-butanone	9.90
2-pentanone	9.69
3-pentanone	9.86
3-methyl-2-butanone	9.64
Cyclopentanone	10.02
Cyclohexanone	9.87
2-hexanone	9.99
3-hexanone	9.90
3-methyl-2-pentanone	9.95
4-methyl-2-pentanone	9.96
4,4-dimethyl-2-pentanone	9.83
2-heptanone	9.69
3-heptanone	9.77
4-heptanone	9.90
Acetophenone	9.97

MASS 27

Source	IP(eV)
Acetyl Acetone	9.93
2-pentanone	9.43
3-methyl-2-butanone	9.48
Cyclopentanone	9.98
Cyclohexanone	10.15
3-hexanone	9.24
3-methyl-2-pentanone	10.38
4-methyl-2-pentanone	9.5 ± 0.1
5-methyl-2-hexanone	9.63
2-heptanone	10.20
3-heptanone	9.86
4-heptanone	9.93

MASS 28

Source	IP(eV)
Acetyl Acetone	10.68
2-butanone	10.65
2-pentanone	10.52
3-pentanone	10.96
3-methyl-2-butanone	10.8 ± 0.1
Cyclopentanone	10.86
Cyclohexanone	10.85
2-hexanone	10.29
3-hexanone	9.39 (not abundant)
3-methyl-2-pentanone	11.02
4-methyl-2-pentanone	10.74
4,4-dimethyl-2-pentanone	10.96
5-methyl-2-hexanone	10.31
2-heptanone	10.54
3-heptanone	10.54
4-heptanone	9.57 (not abundant)

MASS 28

CO

Source	IP(eV)
Acetone	13.2 ± 0.2
Acetyl Acetone	13.7 ± 0.2
2-hexanone	14.7 ± 0.2 ?
3-hexanone	13 ± 1
3-heptanone	13.4 ± 0.2

MASS 29

HCO•

Source	IP(eV)
Acetone	13.83 ± 0.05
4-heptanone	14.4 ± 0.1

Note: The CO IP values were obtained by deconvolution of the upper ranges of the C_2H_4 ionization data. In the same way, the HCO values were obtained by such deconvolution of the C_2H_5 ionization data.

MASS 29

Source	IP(eV)
Acetyl Acetone	9.4 ± 0.1
2-butanone	9.18
2-pentanone	9.38
3-methyl-2-butanone	9.39
Cyclopentanone	9.39
Cyclohexanone	9.41
2-hexanone	9.24
3-hexanone	9.19
3-methyl-2-pentanone	9.68
4-methyl-2-pentanone	9.35
5-methyl-2-hexanone	9.31
2-heptanone	9.35
3-heptanone	9.31
4-heptanone	9.30

MASS 39

Source	IP(eV)
Acetyl Acetone	9.25
2-pentanone	9.38
3-methyl-2-butanone	9.39
Cyclopentanone	9.39
Cyclohexanone	9.11
2-hexanone	9.49
3-hexanone	9.71
3-methyl-2-pentanone	9.66
4-methyl-2-pentanone	10.03
4,4-dimethyl-2-pentanone	9.3 ± 0.1
5-methyl-2-hexanone	9.81
2-heptanone	9.34
3-heptanone	9.86
4-heptanone	9.44
Acetophenone	10.09

MASS 40

Source	IP(eV)
Acetyl Acetone	10.39
2-pentanone	10.60
3-methyl-2-butanone	10.68
Cyclopentanone	11.42 (not abundant)
Cyclohexanone	10.29
2-hexanone	10.31
3-hexanone	10.37
3-methyl-2-pentanone	10.49
4-methyl-2-pentanone	9.98
4,4-dimethyl-2-pentanone	9.83 (not abundant)
5-methyl-2-hexanone	10.73
2-heptanone	10.54
3-heptanone	10.98
4-heptanone	10.49
Acetophenone	10.96

MASS 41

Source	IP(eV)
2-pentanone	8.92
3-methyl-2-butanone	8.95
Cyclopentanone	9.1 ± 0.1
Cyclohexanone	9.10
2-hexanone	8.86
3-hexanone	9.02
3-methyl-2-pentanone	9.35
4-methyl-2-pentanone	8.90
4,4-dimethyl-2-pentanone	9.06
5-methyl-2-hexanone	8.91
2-heptanone	8.82
3-heptanone	9.04
4-heptanone	8.63

MASS 42

Source	IP(eV)
Acetone	9.8 ± 0.1
Acetyl Acetone	9.89
2-butanone	9.93
2-pentanone	10.01
3-methyl-2-butanone	10.38
Cyclopentanone	10.1 ± 0.1
Cyclohexanone	9.90
3-hexanone	9.88
3-methyl-2-pentanone	10.12
4,4-dimethyl-2-pentanone	10.06
3-heptanone	10.39
4-heptanone	10.00
Acetophenone	9.96

Source	IP(eV)
2-hexanone	9.62
4-methyl-2-pentanone	9.63
5-methyl-2-hexanone	9.78
2-heptanone	9.57

MASS 43

Source	IP(eV)
Acetone	10.07
Acetyl Acetone	9.78
2-hexanone	11.7 ± 0.1
3-methyl-2-pentanone	9.31
4-methyl-2-pentanone	10.94
4,4-dimethyl-2-pentanone	9.5 ± 0.1
2-heptanone	10.0 ± 0.1
Acetophenone	9.85

Source	IP(eV)
2-pentanone	8.7 ± 0.1
3-methyl-2-butanone	9.00
3-hexanone	8.9 ± 0.1
2-heptanone	8.5 ± 0.1
3-heptanone	9.23
4-heptanone	8.7 ± 0.1
5-methyl-2-hexanone	8.15

MASS 54

Source	IP(eV)
Acetyl Acetone	10.04
Cyclopentanone	9.74
Cyclohexanone	9.8 ± 0.1
5-methyl-2-hexanone	10.73 (not abundant)
3-heptanone	10.11

MASS 55

Source	IP(eV)
3-methyl-2-pentanone	8.56
4,4-dimethyl-2-pentanone	8.4 ± 0.1
5-methyl-2-hexanone	8.4 ± 0.1
3-heptanone	8.8 ± 0.1

Source	IP(eV)
Acetyl Acetone	9.2 ± 0.1
Cyclopentanone	8.8 ± 0.1
Cyclohexanone	9.0 ± 0.1
3-hexanone	9.6 ± 0.1

MASS 56

Source	IP(eV)
3-hexanone	9.6 ± 0.1
4,4-dimethyl-2-pentanone	9.39
5-methyl-2-hexanone	9.33
2-heptanone	9.54

Source	IP(eV)
Acetyl Acetone	9.98
Cyclopentanone	10.3 ± 0.1
Cyclohexanone	10.6 ± 0.1
3-methyl-2-pentanone	10.02
4-methyl-2-pentanone	9.96
3-heptanone	10.24

MASS 57

Source	IP(eV)
3-methyl-2-pentanone	8.55
4-methyl-2-pentanone	8.9 ± 0.1
4,4-dimethyl-2-pentanone	8.8 ± 0.1

Source	IP(eV)
Acetyl Acetone	10.09
2-butanone	10.2 ± 0.1
3-hexanone	10.24
5-methyl-2-hexanone	10.07

129

MASS 58

Source	IP(eV)
Acetyl Acetone	9.24
Cyclohexanone	10.30
2-hexanone	11.28 (not abundant)
3-hexanone	10.6 ± 0.1
4-methyl-2-pentanone	10.32
4,4-dimethyl-2-pentanone	9.9 ± 0.1
5-methyl-2-hexanone	9.87
2-heptanone	10.02

MASS 59

Source	IP(eV)
4,4-dimethyl-2-pentanone	10.1 ± 0.1
2-heptanone	9.58

MASS 70

Source	IP(eV)
Cyclohexanone	11.7 ± 0.1

MISCELLANEOUS

Mass	Formula	Source	IP(eV)
71	C_4H_7O	3-hexanone	9.48
71	C_5H_{11}	5-methyl-2-hexanone	9.59
		4,4-dimethyl-2-pentanone	8.7 $\pm$ 0.1
72	C_4H_8O	Acetyl Acetone	9.6 $\pm$ 0.1
		3-methyl-2-pentanone	10.02
		4-methyl-2-pentanone	10.72
85	C_5H_9O	3-methyl-2-butanone	9.72
85	$C_4H_5O_2$	Acetyl Acetone	9.97
86	$C_5H_{10}O$	5-methyl-2-hexanone	8.97