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THE OCCURRENCE OF THE H$_3^+$ ION IN THE MASS SPECTRA OF ORGANIC COMPOUNDS

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ABSTRACT

The H$_3^+$ ion is shown to be a normal component of low yield in the fragmentation pattern of organic compounds (except C$_2$H$_2$). The pattern of H$_3^+$ is tabulated for the 70 eV mass spectrum of each of 33 compounds of various types. Specific studies of the energetics of formation of H$_3^+$ from CH$_4$, C$_2$H$_6$ and CH$_3$Cl, and of D$_3^+$ from CD$_4$ were conducted. The H$_3^+$ ion is shown to be derived from two sources, a low initial kinetic energy component which arises from fragmentation of the singly charged molecular ion and a high initial kinetic energy component whose AP and kinetic energy release is consistent with fragmentation of the doubly charged molecular ion. Systematic variations of H$_3^+$ pattern factors with carbon number are shown for the n-alkanes and l-alkenes and with halogen type for the series of methyl halides.
I. INTRODUCTION

No investigation of the occurrence of $H_3^+$ ions in the mass spectra of organic compounds has been made except for an early study by Smith\textsuperscript{1}. In his investigation, Smith showed that $H_3^+$ ions occurred in the mass spectrum of methane, the intensity of the $H_3^+$ peak was linear with pressure, and the appearance potential, AP, of $H_3^+$ was reported to be 25.3±1 eV, about two electron volts lower than the AP of $H_2^+$ from methane.

In the present investigation the occurrence of $H_3^+$ in the mass spectrum of methane has been restudied and the study extended to other organic compounds. In the present limited survey, no organic compound other than acetylene failed to exhibit a mass peak due to the occurrence of $H_3^+$.

II. EXPERIMENTAL

The present work was done with a Consolidated Electrodynamics Corp. Model 21-103B mass spectrometer. Modifications to increase the sensitivity of the recording system, the vacuum capabilities of the instrument, and modifications to record directly ionization efficiency curves on an X-Y recorder have been described previously\textsuperscript{2,3}. In the present investigation, negative-repeller studies were performed by use of batteries in the modified repeller circuit. Under these conditions peaks were scanned by a motor drive of the magnet current control. Repeller potentials were measured with a battery operated vacuum tube voltmeter which was at the potential of the ion source. Metastable suppressor cutoff curves were determined with a multiple decade potential divider. In the first three decades, the resistors were trimmed to an accuracy of 0.01%. The fourth stage, a ten turn potentiometer, had a linearity of
0.1%. In all work reported here, an ionizing electron current of 38 μA was used. For AP determinations, owing to the low intensity of these peaks, equal repeller potentials of ~ 0.01 Vₘ were used. Under these conditions secondary effects in the ion source, e.g., space charge effects and charge exchange from ions produced at the anode, are not observed. The electron energy scale was corrected by comparison with a standard (usually He) introduced into the gas mixture so the intensity of the respective peaks at about 50 eV were approximately equal. At high metastable suppressor voltages (near cutoff) the peaks become so narrow the X-Y recording procedure could not be used owing to the possibility of drifting off the peak while scanning the electron energy scale. The ionization efficiency curves of these peaks were determined on a point to point basis, scanning the peak magnetically at each predetermined electron energy.

The hydrocarbons used were Phillips Research Grade hydrocarbons. The alkyl halides were ACS Reagent Grade chemicals. The methane used was >99.99% pure and was obtained from Pacific Oxygen Co. The CD₄ was obtained from the Merck Sharp and Dohme Co. The CH₃F used was synthesized and purified by gas chromatography.

III. RESULTS AND DISCUSSION

In Fig. 1 is shown the linearity with inlet system pressure of H₃⁺ from CH₄, D₃⁺ from CD₄ and H₃⁺ from C₂H₆. The peaks due to CH₄⁺ and H₂⁺ from CH₄ are also shown. All are linear with pressure, hence the formation of H₃⁺ is assumed to occur by a unimolecular process. As a further check on this point, the ratio of M/q = 5 to M/q = 6 in CD₄ (D₂H⁺/D₃⁺) was measured and found to be 0.020±0.001. This corresponds to an H atom impurity of ~0.7% in the CD₄. An equimolar...
mixture of CH₄ and CD₄ showed the same ratio (0.020±0.001) of M/q = 5 to M/q = 6, confirming that all three atoms in D₃⁺ arise from one molecule of CD₄. These experiments confirm the earlier conclusion of Smith in regard to the unimolecular character of H₃⁺ production from methane.

In Table 1 are shown the yields of H₃⁺ ions at a nominal ionizing voltage of 70 V from a variety of organic molecules. The measurements were made by scanning M/q = 2 at an ion accelerating voltage, V_A, of 3000 V and M/q = 3 at a voltage of 2000 volts. Since each of these ions is formed with components possessing high initial kinetic energy (vide infra) the intensity ratio of H₃⁺/H₂⁺ found for each compound applies only to measurements made under essentially identical conditions and should not be used on an absolute basis. They are useful in indicating trends and order of magnitude expectations of H₃⁺ yields. Since our own files of mass spectral data on these compounds were obtained under conditions in which M/q = 2 was scanned at 3000 V, these data have been used to relate H₃⁺ to the total ion yield of these compounds. (If the A.P.I. Mass Spectral Data are used for this purpose, the H₂⁺ yields will, in general, be found to be lower than those used in the present calculations owing to differences in instrument operating procedures).

For the data in Table 1, each of the compounds was studied at three pressures, usually 25, 50, and 100 μm inlet pressure. In all cases the peak sensitivity of H₃⁺ and the intensity ratio of H₃⁺ to H₂⁺ were independent of pressure.

The only organic compound investigated in which no H₃⁺ was found was C₂H₂ (not listed in Table 1) from which the formation of H₃⁺ by a unimolecular process is impossible. The ratio of M/q = 3 to M/q = 2 found from C₂H₂ was
0.00030±0.00005. If all the M/q = 3 peak is due to HD, this corresponds to a deuterium content \([D/(H + D)]\) of 0.015%. This is equal to the natural abundance of deuterium from various sources within the experimental error. No \(H_3^+\) was observed in the mass spectrum of \(H_2O\) nor was any \(D_3^+\) observed in the mass spectrum of \(D_2O\). The yield of \(D_3^+\) in the mass spectrum of \(ND_3\) was about 30% of the yield from an identical pressure of \(CD_4\). Because of the low intensity, \(ND_3\) was not investigated further.

The compounds \(CH_4\), \(CD_4\), \(C_2H_6\), and \(CH_3Cl\) were selected for more detailed study since these compounds are relatively simple and considerable information is available on the energetics of these compounds. Fig. 2 shows voltage discrimination curves of \(H_3^+\) from \(CH_4\) and \(C_2H_6\) and of \(D_3^+\) from \(CD_4\). The extreme slope of these curves is indicative of ions with high initial kinetic energy. One may also infer from these curves that \(H_3^+\) from \(CH_4\) has less initial kinetic energy than does \(H_3^+\) from \(C_2H_6\). The slope of \(D_3^+\) from \(CD_4\) is also less than that of \(H_3^+\) from \(CH_4\) indicating slightly less initial kinetic energy for \(D_3^+\). These curves are not sensitive functions of the initial kinetic energy, but calculations of discrimination due to initial kinetic energy by the method of Berry show that the \(H_3^+\) from \(CH_4\) curve can be approximated with an initial kinetic energy of \(H_3^+\) equal to 0.5 eV, that of \(D_3^+\) from \(CD_4\) with an initial kinetic energy of \(D_3^+\) equal to about 0.35 eV, and that of \(H_3^+\) from \(C_2H_6\) with an initial kinetic energy of between 5 and 6 eV.

Other methods of evaluating initial kinetic energy are the deflection method, measurement of satellite peaks at low ion accelerating voltages, peak cutoff curves with an ion-retarding plate at the ion collector, negative-repeller cutoff curves of the ion peak, and peak cutoff curves measured by
retarding the ions on one of the ion accelerating slits of the ion source. This last method is the most sensitive for ions with low initial kinetic energy. The equipment used could not, however, be adapted for application of this method.

In the present investigation the methods used were: 1) the measurement of satellite peaks at low ion accelerating voltage, 2) the measurement of the negative repeller cutoff, and 3) the method of retarding ions at the collector.

The measurement of satellite peaks was found to be of limited utility because of low intensity at low ion accelerating voltages (see Fig. 2) and the lack of resolution of any satellite peaks at \( H_3^+ \) in the mass spectrum of \( CH_4 \) or \( D_3^+ \) in the mass spectrum of \( CD_4 \). Satellite peaks were observed at \( M/q = 3 \) from \( C_2H_6 \) and \( CH_3Cl \), and these gave values of the initial kinetic energy of the respective high KE components comparable to the values found by the other methods.

In the negative repeller cutoff method, the difference in the repeller cutoff voltage of an ion formed with thermal initial kinetic energy distribution and one formed with higher initial kinetic energy is equal to twice the initial kinetic energy. This results from the location of the ionizing electron beam being approximately midway between the repellers and the ion-source exit slit. Because of this placement, the ionizing electron energy is determined by the potential applied between the filament and the ion source plus approximately one-half the repeller potential. Owing to the uncertainty in this factor, the negative repeller cutoff method is not reliable at low ionizing voltages since the applied ionizing voltage must be corrected each time the repeller potential is changed. At higher ionizing voltages, where the ionization-efficiency curve
is relatively flat, this uncertainty is not a critical factor in the measurements.

In the method of retarding ions at the collector, the metastable suppressor was used as a retarding grid. The maximum potential applied to the metastable suppressor must be sufficient to retard those ions of highest initial kinetic energy. Since the metastable suppressor is an einzel lens system, it has both a focusing action (the apparent collector slitwidth narrows as the potential on the metastable suppressor is increased) and a potential well of depth such that the potential actually applied to the ions is a factor of 0.973 times the potential applied to the plates. This factor was determined by Kandel\textsuperscript{9} for the metastable suppressor in the CEC instrument, and the measurements reported here are in agreement with this factor.

If the maximum potential applied to the metastable suppressor is defined as $1.0000 \, V_{mss}$ and the fraction of this potential required to completely retard the ions is defined as $f_{mss}$, then from the retarding curves of an ion formed with thermal initial kinetic energy and one formed with higher initial kinetic energy, the difference in initial kinetic energy of the two ions is given by equation (1).

$$\textit{K.E.} = 0.973 \, V_{mss} \left( \Delta f_{mss} \right)$$

(1)

In this equation, $\Delta f_{mss}$ is the difference between the cutoff fraction of a high initial kinetic energy ion and one whose initial kinetic energy is thermal. In measuring these cutoff curves, the ion accelerating voltage, the ionizing voltage, the repeller potential and the gas mixture were all kept constant over the duration of both determinations. The peaks were scanned by sweeping with the magnetic field. The method is most sensitive at low ion accelerating voltages
but for reasons of intensity, its use at low voltage is difficult. The present experiments were made at \( V_A = 2000 \text{ V} \) and \( V_{mss} = 2097 \text{ V} \). Under these conditions both \( D_3^+ \) from \( \text{CD}_4 \) and \( H_3^+ \) from \( \text{C}_2\text{H}_6 \) and \( \text{CH}_3\text{Cl} \) could be studied under identical conditions. In order to compare curves on the same basis, the peak intensities at various values of \( \varepsilon_{mss} \) were normalized with respect to the peak intensity at \( 0.960 \text{ V}_{mss} \) which was set equal to 100. The accuracy of determining \( \Delta \varepsilon_{mss} \) is about \( \pm 0.00005 \) for ions of reasonable intensity. With \( V_{mss} = 2097 \text{ V} \) the probable error in measurement of the initial kinetic energy is \( \pm 0.1 \text{ eV} \).

The methods have been checked by measurement of the initial kinetic energy of the \( M/q = 15 \) satellite peak in the mass spectrum of propane. Olmsted, Street, and Newton using the satellite method and a 0.75 mm collector slit-width, found this peak to be formed with 2.65 eV of initial kinetic energy. Newton and Sciamanna using a 0.025 mm collector slit-width with the satellite method found 2.85±0.05 eV. R. Fuchs with an absolute calibration of the deflection method found 2.71±0.05 eV. Earlier values from 2.2 to 2.9 eV are summarized by Fuchs and Taubert who assumed an average value of 2.50 eV for the initial calibration of the deflection method. The methods used in this investigation give values of 2.75±0.1 eV by the metastable suppressor cutoff method and 2.9±0.1 eV by the negative repeller method. It was concluded that these methods yield results consistent with other measurements.

Fig. 3 shows the negative repeller cutoff curves of \( \text{H}_3^+ \) and \( \text{D}_3^+ \) from \( \text{CH}_4 \) and \( \text{CD}_4 \) respectively at an ionizing electron energy of 70 eV. They show both \( \text{H}_3^+ \) and \( \text{D}_3^+ \) to have a large contribution (>90%) of low initial kinetic energy ions with each having small (<10%) component of high kinetic energy ions. It is difficult to analyze these curves to obtain initial kinetic energies of
the low energy component but the shapes suggest values of \( \sim 0.7 \text{ eV} \) for \( \text{H}_3^+ \) from \( \text{CH}_4 \) and \( \sim 0.5 \text{ eV} \) for \( \text{D}_3^+ \) from \( \text{CD}_4 \). The high initial kinetic energy components showed energies of 4.9 and 3.9 eV respectively.

Fig. 4 shows the metastable suppressor cutoff curves of \( \text{D}_3^+ \) from \( \text{CD}_4 \) compared to \( ^{22}\text{Ne}^+ \) as a thermal ion standard (a small \( \text{CD}_5^+ \) contribution to \( M/q = 22 \) was separated). At a corrected electron energy of 81 eV these curves show the \( \text{D}_3^+ \) to have a small ( \( \sim 10\% \) ) component of ions of initial kinetic energy \( 4.0 \pm 0.1 \text{ eV} \) and a large component of ions near thermal ( \( \leq 0.1 \text{ eV} \) ). There is no evidence of any significant contribution of ions of intermediate initial kinetic energy. A small contribution of such ions would not be detectable.

Fig. 5 shows the negative repeller cutoff curves of \( \text{H}_3^+ \) from \( \text{C}_2\text{H}_6 \) and \( \text{CH}_3\text{Cl} \) respectively at an ionizing electron energy of 90 eV. The cutoff curves of the parent ions of each are shown as standards for thermal ions. Both curves show large contributions of components with high initial kinetic energy and no indication of any appreciable contribution from ions of lower initial kinetic energy. Initial kinetic energies of \( 4.3 \pm 0.2 \) and \( 4.1 \pm 0.2 \) for \( \text{H}_3^+ \) from \( \text{C}_2\text{H}_6 \) and \( \text{CH}_3\text{Cl} \) respectively were derived from these curves.

Figs. 6 and 7 show the metastable suppressor cutoff curves of \( \text{H}_3^+ \) from \( \text{C}_2\text{H}_6 \) and \( \text{CH}_3\text{Cl} \) respectively. The cutoff of \( \text{He}^+ \) ions is used as a thermal ion standard in each case. The cutoff curves of \( \text{H}_3^+ \) (and \( \text{He}^+ \)) were determined at corrected ionizing electron energies of about 83 eV and at about 7 eV above the appearance potential. At electron energies of 83 eV, each shows only a high kinetic energy component but a few volts above the appearance potential, each shows the major component to be near thermal ( \( \leq 0.2 \text{ eV} \) ) with a small contribution of a high initial kinetic energy component. Curves (not shown) determined at
electron energies a few volts higher (∼ 37 eV) show a rapid increase with
increase in ionizing voltage of the high kinetic energy component and no
indication of any intermediate energy components. The high initial kinetic
energy component of $H_3^+$ from $C_2H_6$ shows an energy of 3.8±0.1 eV and that from
$CH_3Cl$ an energy of 3.7±0.1 eV.

Ionization efficiency curves for formation of $H_3^+$ from $CH_4$ and $D_3^+$
from $CD_4$ are shown in Fig. 8. The overall shape of the curves for $H_3^+$ from
the other compounds investigated in detail are similar, each showing a fairly
weak onset followed by a strong rise to a broad plateau. The use of the
metastable suppressor makes possible the separation of those $H_3^+$ ions possessing
high initial kinetic energy compared to those from the mixed species. Fig. 9
shows the separate ionization efficiency curves of $D_3^+$ from $CD_4$ at $f_{mss} = 0.97$
where both high and low initial kinetic energy species are collected, showing
an AP of 25.5 eV, and the curve at $f_{mss} = 0.98535$ where only the high initial
kinetic energy ions reach the collector. Points on the latter curve show
considerable scatter because of the poor signal to noise ratio with this low
intensity peak. Several determinations of this curve, using both an extrapolated
initial appearance and a square root extrapolation, yield a value of 35.5±2 eV
for the appearance potential of the $D_3^+$ ions of high initial kinetic energy
from $CD_4$.

Figs. 10 and 11 show the ionization efficiency curves for the high and
the combined high and low initial kinetic energy $H_3^+$ ions from $C_2H_6$ and $CH_3Cl$
respectively. In each case a square root extrapolation is included with the
curve of the high kinetic energy component. While the combined AP curve shows
a small contribution due to $HD^+$ below the AP of $H_3^+$ in each case, no such
contribution is seen in the high KE curves and points below the AP's (shown by the arrows) are zero within the limits of detectability.

In Table 2 the appearance potentials of $H_3^+$ for several compounds are shown together with data obtained for the high initial kinetic energy of the $H_3^+$ fragment. In those cases where the ratio of intensities of $H_3^+$ to $H_2^+$ is low, the HD$^+$ contribution at $M/q = 3$ interferes with the determination of the onset of the initial rise of the $H_3^+$ peak from fragmentation of the compound. The uncertainty in the AP is necessarily larger in these cases. In all cases except $D_3^+$ from CD$_4$, the onset of He$^+$ ions from an He internal standard was used to calibrate the voltage scale. In the case of CD$_4$, $^{22}\text{Ne}^+$ was used as a standard. The peak due to Ne$^+$ at $M/q = 22$ was separated from the small CD$_5^+$ peak at the same nominal mass when a 0.5 mm collector slit was used. The $D_3^+$ peak was also separated from the C$^{+2}$ peak, though in any case this would not interfere with the appearance potential determination of $D_3^+$ since C$^{+2}$ has a much higher AP. The AP's of $H_3^+$ from CH$_4$ and of $D_3^+$ from CD$_4$ are equal within experimental error and agree with the value of 25.3±1 eV reported by Smith$^1$.

In Table 1 the yields of $H_3^+$ and $H_2^+$ appear to be unrelated. This is expected since it is highly improbable that $H_2^+$ and $H_3^+$ would arise from the same set of excited states of the molecule ion, or if they did, that the relative dissociation probabilities leading to these two products would be constant from one compound to another. In Fig. 12 the yields of $H_2^+$ and $H_3^+$ from a series of normal hydrocarbons are plotted. The $H_2^+$ yield from n-alkanes decreases slowly with increase in carbon number from C$_1$ to C$_8$. The $H_3^+$ yield increases sharply from methane to ethane and then falls off rapidly with
increasing carbon number. In the series of 1-alkenes, the yield of \( \text{H}_3^+ \) from ethylene is similar in magnitude to that from methane but the yield from propylene and higher alkenes does not differ significantly from the yield from n-alkanes of the same carbon number. The data in Table 1 also indicates a small effect of structure. The yield of \( \text{H}_3^+ \) from the alkanes decreases as the alkanes become more branched. The butenes show a maximum yield from the 2-butenes and a lesser yield when the double bond is at a terminal carbon in 1-butene or isobutene. The effects are small however, and data from many more compounds would be necessary to evaluate detailed structural effects.

Fig. 13 shows the yield of \( \text{H}_3^+ \) from each compound in the series of methyl halides. Methane is included for comparison. The yield of \( \text{H}_2^+ \) decreases slowly in this series. The \( \text{H}_3^+ \) yield from \( \text{CF}_4 \) is similar in magnitude to that from \( \text{CH}_4 \), while \( \text{CH}_3\text{Cl} \) shows a marked increase in \( \text{H}_3^+ \) yield over that observed in \( \text{CH}_3\text{F} \). The yield from \( \text{CH}_3\text{Br} \) is a factor of 2 below that of \( \text{CH}_3\text{Cl} \) and the yield from \( \text{CH}_3\text{I} \) is a factor of 17 below that of \( \text{CH}_3\text{Br} \). While the \( \text{H}_3^+ \) yield in this series shows no relation to the \( \text{H}_2^+ \) yield, the yields of \( \text{H}_2\text{X}^+ \) ions (also shown in Fig. 13) show a variance similar to that observed for \( \text{H}_3^+ \) ions. The yields of \( \text{H}_2\text{X}^+ \) ions were calculated from measurements made at \( M/q = 21 \) for \( \text{H}_2\text{F}^+ \) from \( \text{CH}_3\text{F} \), at \( M/q = 39 \) for \( \text{H}_2\text{Cl}^+ \) from \( \text{CH}_3\text{Cl} \) (corrected for the abundance of \( ^{37}\text{Cl} \)), at \( M/q = 83 \) for \( \text{H}_2\text{Br}^+ \) from \( \text{CH}_3\text{Br} \) (corrected for the abundance of \( ^{81}\text{Br} \)), and at \( M/q = 129 \) for \( \text{H}_2\text{I}^+ \) from \( \text{CH}_3\text{I} \). These peaks were each linear with pressure from 25 to 100 \( \mu \text{m} \) inlet pressure. The descrimination due to initial kinetic energy will be much less for \( \text{H}_2\text{X}^+ \) than for \( \text{H}_3^+ \) since the heavier \( \text{H}_2\text{X}^+ \) fragments will carry less of any initial kinetic energy released in the production of these ions than is the case for the lighter \( \text{H}_3^+ \) fragment. Therefore the yields of \( \text{H}_2\text{X}^+ \) more nearly represent absolute yields relative to the total ionization than do the yields of \( \text{H}_3^+ \).
From the data given, it is concluded that there are two mechanisms for producing $H_3^+$ ions from organic compounds. One leads to an ion of low initial kinetic energy and the other to an ion of high initial kinetic energy. The latter has an AP some 6 to 10 eV higher than the former. It is assumed that the low kinetic energy ion is formed from fragmentation of a singly charged molecular ion and the high kinetic energy ion from a doubly charged molecular ion. From thermodynamic data, the minimum AP for formation of $H_3^+$ by each of these processes can be calculated. It is assumed that the reactions occurring are the following:

$$H_3CX + e^- \rightarrow H_3^+ + CX + 2e^- \quad (2)$$

$$H_3CX + e^- \rightarrow H_3^+ + CX^+ + 3e^- \quad (3)$$

Calculations were performed using heats of formation of the species involved compiled by Franklin, Dillard, Rosenstock, Herron, Draxl, and Field\textsuperscript{15}. Using the heats of formation in eV per molecule, the appearance potential, assuming zero initial kinetic energy release, can be calculated.

$$AP (H_3^+) = \Delta H_f (CX) + \Delta H_f (H_3^+) - \Delta H_f (CH_2X) \quad (4)$$

In the case of the doubly charged fragmentation mechanism, the first term on the right becomes $\Delta H_f (CX^+)$. The heat of formation of $H_3^+$ was calculated from theoretical calculations of Conroy\textsuperscript{16} on $H_3^+$, from which the value $A = 4.73$ eV was derived for the proton affinity of hydrogen. This value is higher than the experimental values of 3.0 derived from data on proton scattering in $H_2$\textsuperscript{17} and from a study of ion-molecule reactions of $H_2^+$\textsuperscript{18}. Use of $A = 4.73$ eV leads to a heat of formation of $H_3^+$ of 11.12 eV.
The calculated AP values are summarized in Table 3. To each of these is added the initial kinetic energy release, T, to obtain the minimum AP which should be observed, assuming $H_3^+$ to be formed in the lowest vibrational level of the $^1A_1$ ground state and CX (or CX$^+$) to be formed in the lowest vibrational level of the ground state. For the compounds studied, the calculated and observed AP's of the high initial kinetic energy $H_3^+$ component agree well with the values calculated by the doubly charged ion mechanism. In the case of $C_2H_6$ the observed AP of the high initial kinetic energy component of $H_3^+$ is, within the experimental uncertainty, equal to the value of 30.3±0.3 eV found by Olmsted, Street and Newton for the formation of high initial kinetic energy $CH_3^+$ ions. It is concluded that the high initial kinetic energy ions result from fragmentation of the doubly charged molecular ion.

The low initial kinetic energy component must be formed by fragmentation of a singly charged ion. The difference between the lowest calculated AP and that observed for this component, some 8 to 10 eV, suggests that the molecular ion is formed initially in a highly excited state. The experimental results suggest no disposition of this excess energy, but in all cases it is considerably higher than the C-X bond energy. Several possibilities are obvious, i.e., emission of light from an excited state of CX, fragmentation of CX with release of kinetic energy, and fragmentation of CX with C being formed in an excited state. In the cases of CD$_4$ and CH$_3$Cl, the formation of D or Cl respectively in an excited state can be eliminated since in each case the energy level of the first excited state plus the C-X bond energy is higher than the excess energy available.

The wide variance in yields of $H_3^+$ observed from various compounds as illustrated in Fig. 12 and 13 can arise from differences in relative yields of
H$_3^+$ from the two independent mechanisms. In the cases examined, CD$_4$ and C$_6$H$_6$ show low yields of H$_3^+$ (at $V_e = 70$ V) but most of this yield is due to the low initial kinetic energy component. The higher yield of H$_3^+$ at $V_e = 70$ V from C$_2$H$_6$ and CH$_3$Cl respectively is due to the increased yield of the high initial kinetic energy component. Any significant correlation would require the separate consideration of these respective yields. Experimentally, other than an order of magnitude estimation, no method of measuring the separate yields was found.

The equality of AP's for the high kinetic energy ions H$_3^+$ and CH$_3^+$ from C$_2$H$_6$ suggests the doubly charged C$_2$H$_6^{+2}$ can fragment by at least these two paths. Olmsted, Street, and Newton$^5$ found the kinetic energy of the CH$_3^+$ satellite to be 2.45 eV, and new measurements by the metastable suppressor cutoff method yield 2.65 eV. The latter figure results in $T = 5.30$ eV of kinetic energy release and corresponds to a separation of charges of 2.7 Å. For separation into H$_3^+$ and C$_2$H$_3^+$, $T = 4.2$ eV and the separation of charges is 3.4 Å. For CH$_3$Cl, Olmsted, Street, and Newton found the satellite of CH$_3^+$ to have an initial kinetic energy of 4.15 eV, corresponding to a $T$ of 5.9 eV and a separation of charges of 2.4 Å. For separation into H$_3^+$ and CCl$_3^+$, $T = 3.9$ eV and the separation of charges is 3.7 Å. In each case the separation of charges is larger for fragmentation into H$_3^+$ + CX$^+$ than for fragmentation into CH$_3^+$ + X$. This is qualitatively the result that would be expected from primitive concepts of the transition states in the two cases, H$_3^+$ -C-X$^+$ and CH$_3^+$ -X$^+$.  

Fuchs and Taubert$^{13}$ showed that the H$_2^+$ ions from hydrocarbons have components of high initial kinetic energy. A metastable suppressor cutoff curve
of \( \text{H}_2^+ \) from \( \text{C}_2\text{H}_6 \) showed a component of initial kinetic energy equal to 3.7±0.1 eV. This component had an AP of 31.1±1 eV. Assuming the fragmentation process to be \( \text{C}_2\text{H}_6^{+2} \) fragmenting to \( \text{H}_2^+ \) and \( \text{C}_2\text{H}_4^+ \), \( T = 4.0 \) eV and the separation of charges, 3.6 Å, is slightly larger than that calculated for separation into \( \text{H}_3^+ \) and \( \text{C}_2\text{H}_3^+ \). The suggestion implied by this data is that the same electronic state of \( \text{C}_2\text{H}_6^{+2} \) can fragment by at least three independent paths. While this suggestion is consistent with the available data, it does not represent a firm conclusion.

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REFERENCES


4. "Mass Spectral Data", American Petroleum Institute Research Project 44; B. J. Zwolinski, Director, Texas A & M University, College Station, Texas.


17. J. H. SIMONS, C. M. FONTANA, E. E. MUSCHLITZ, JR.; and S. R. JACKSON,


19. V. I. VEDENEYEV, L. V. GURVICH, V. N. KONDRAT'YEV, V. A. MEDVEDEV, and
    YE. L. FRANKEVITCH, Bond Energies, Ionization Potentials and Electron
FIGURE LEGENDS

Fig. 1. Variation of peak sensitivity (peak intensity/pressure) with pressure for M/q = 2, 3 and 16 from CH₄, M/q = 6 from CD₄, and M/q = 3 from C₂H₆.
Conditions: Iₑ = 38.5 μA; Vₑ = 70 V; Vₐ = 0.0113 Vₐ; M/q = 2 scanned at Vₐ = 3000 V, 3 at 2000 V, 6 at 2000 V and 16 at 2840 V.

Fig. 2. Ion accelerating voltage discrimination curves of H⁺ ions from CH₄ and C₂H₆, and D⁺ ions from CD₄.

Fig. 3. Repeller cutoff curves of H⁺ ions from CH₄ and D⁺ ions from CD₄.
Conditions: Vₑ = 70 V; Vₐ = 3000 V; repellers equal; magnetic scan.

Fig. 4. Metastable suppressor cutoff curves of ²²Ne⁺ ions and D⁺ ions from a mixture of ²²Ne and CD₄. Conditions: Vₐ = 2000 V; repellers equal at 0.008 Vₐ; 1.000 Vₐ = 2097 V; Vₑ = 81 V; magnetic scan.

Fig. 5. Repeller cutoff curves of H⁺ ions from C₂H₆ and H⁺ ions from CH₃Cl.
Conditions: Vₑ = 90 V; Vₐ = 3000 V; repellers equal; magnetic scan.

Fig. 6. Metastable suppressor cutoff curves of He⁺ ions and H⁺ ions from a mixture of 1% He gas in C₂H₆ at corrected ionizing electron energies of 83 eV and 33 eV. Conditions: Vₐ = 2000 V; repellers equal at 0.01 Vₐ; 1.000 Vₐ = 2097 V; magnetic scan.

Fig. 7. Metastable suppressor cutoff curves of He⁺ ions and H⁺ ions from a mixture of 1% He gas in CH₃Cl at corrected ionizing electron energies of 83 eV and 32.3 eV. Conditions: Vₐ = 2000 V; repellers equal at 0.01 Vₐ; 1.000 Vₐ = 2097 V; magnetic scan.

Fig. 8. Ionization efficiency curves for the formation of H⁺ from CH₄, and D⁺ from CD₄. Conditions: Vₐ = 3000 V; Vₐ = 0.0065 Vₐ; inlet pressure = 100 μm. Voltage scale corrected by appearance potentials of He⁺ (CH₄) and ²²Ne⁺ (CD₄).
Fig. 9. Ionization efficiency curves for formation of $D_3^+$ ions from $CD_4$. Variation of curves with fraction of metastable suppressor voltage applied at collector. Conditions: $V_A = 2000 \text{ V}$; repellers equal at $0.008 V_A$; $1.000 \text{ V}_{\text{mss}} = 2097 \text{ V}$; magnetic scan. Electron energy scale corrected to first appearance of $D_3^+$ at $25.5 \text{ eV}$ with $f_{\text{mss}} = 0.970$.

Fig. 10. Ionization efficiency curves for formation of $He^+$ and $H_3^+$ ions from a mixture of $1\%$ He in $C_2H_6$. Variation of $H_3^+$ curves with fraction of metastable suppressor voltage applied at collector. Conditions: $V_A = 2000 \text{ V}$; repellers equal at $0.01 V_A$; $1.000 \text{ V}_{\text{mss}} = 2097 \text{ V}$; magnetic scan. Electron energy scale corrected to first appearance of $He^+$ at $24.6 \text{ eV}$ with $f_{\text{mss}} = 0.980$.

Fig. 11. Ionization efficiency curves for formation of $He^+$ and $H_3^+$ from a mixture of $1\%$ He in $CH_3Cl$. Variation of $H_3^+$ curves with fraction of metastable suppressor voltage applied at collector. Conditions: $V_A = 2000 \text{ V}$; repellers equal at $0.01 V_A$; $1.000 \text{ V}_{\text{mss}} = 2097 \text{ V}$; magnetic scan. Electron energy scale corrected to first appearance of $He^+$ at $24.6 \text{ eV}$.

Fig. 12. Variation of yields of $H_2^+$ and $H_3^+$ in the n-alkanes and of $H_3^+$ in the 1-alkenes with carbon number.

Fig. 13. Variation of yields of $H_2^+$, $H_3^+$, and $H_2X^+$ in the methyl halides.
Table 1. Observed Yields of $H_3^+$ Ion from Various Compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$H_3^+/H_2^+$</th>
<th>Pattern $H_3^+$</th>
<th>Pattern $H_2X^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkanes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.0088</td>
<td>0.0038</td>
<td></td>
</tr>
<tr>
<td>CD$_4$</td>
<td>0.0088</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>0.143</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.146</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>0.065</td>
<td>0.0076</td>
<td></td>
</tr>
<tr>
<td>i-C$<em>4$H$</em>{10}$</td>
<td>0.067</td>
<td>0.0072</td>
<td></td>
</tr>
<tr>
<td>neo-C$<em>5$H$</em>{12}$</td>
<td>0.037</td>
<td>0.0026</td>
<td></td>
</tr>
<tr>
<td>i-C$<em>5$H$</em>{12}$</td>
<td>0.033</td>
<td>0.0033</td>
<td></td>
</tr>
<tr>
<td>n-C$<em>5$H$</em>{12}$</td>
<td>0.038</td>
<td>0.0041</td>
<td></td>
</tr>
<tr>
<td>n-C$<em>6$H$</em>{14}$</td>
<td>0.029</td>
<td>0.0021</td>
<td></td>
</tr>
<tr>
<td>n-C$<em>7$H$</em>{16}$</td>
<td>0.017</td>
<td>0.0012</td>
<td></td>
</tr>
<tr>
<td>n-C$<em>8$H$</em>{18}$</td>
<td>0.013</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>2,2,4-trimethyl-pentane</td>
<td>0.016</td>
<td>0.0012</td>
<td></td>
</tr>
<tr>
<td><strong>Alkenes, polyolefins, and aromatics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>0.0097</td>
<td>0.0032</td>
<td></td>
</tr>
<tr>
<td>C$_3$H$_4$ (methyl acetylene)</td>
<td>0.029</td>
<td>0.0049</td>
<td></td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>0.076</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>1,2-C$_4$H$_6$</td>
<td>0.025</td>
<td>0.0046</td>
<td></td>
</tr>
<tr>
<td>1,3-C$_4$H$_6$</td>
<td>0.018</td>
<td>0.0033</td>
<td></td>
</tr>
<tr>
<td>1-C$_4$H$_8$</td>
<td>0.030</td>
<td>0.0055</td>
<td></td>
</tr>
<tr>
<td>2-C$_4$H$_8$ (cis)</td>
<td>0.036</td>
<td>0.0079</td>
<td></td>
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</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\text{H}_3^+/\text{H}_2^+$ $^a$</th>
<th>Pattern $\text{H}_3^+$ $^b$</th>
<th>Pattern $\text{H}_2^+$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkenes, polylefins, and aromatics, continued</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-C$_4$H$_8$ (trans)</td>
<td>0.036</td>
<td>0.0075</td>
<td></td>
</tr>
<tr>
<td>i-C$_4$H$_8$</td>
<td>0.030</td>
<td>0.0061</td>
<td></td>
</tr>
<tr>
<td>2-methylbutene-2</td>
<td>0.025</td>
<td>0.0036</td>
<td></td>
</tr>
<tr>
<td>hexene-1</td>
<td>0.017</td>
<td>0.0019</td>
<td></td>
</tr>
<tr>
<td>2,2,4-trimethyl-pentene-1</td>
<td>0.013</td>
<td>0.0014</td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>0.037</td>
<td>0.0025</td>
<td></td>
</tr>
<tr>
<td>Misc. compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$F</td>
<td>0.017</td>
<td>0.0051</td>
<td>0.0024 ($\text{H}_2^\text{F}^+$)</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>0.215</td>
<td>0.043</td>
<td>0.026 ($\text{H}_2^\text{Cl}^+$)</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>0.200</td>
<td>0.024</td>
<td>0.031 ($\text{H}_2^\text{Br}^+$)</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>0.016</td>
<td>0.0014</td>
<td>0.015 ($\text{H}_2^\text{I}^+$)</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>0.053</td>
<td>0.028</td>
<td>0.11 ($\text{H}_3^\text{O}^+$)</td>
</tr>
<tr>
<td>C$_2$H$_5$OH</td>
<td>0.076</td>
<td>0.025</td>
<td>1.3 ($\text{H}_3^\text{O}^+$)</td>
</tr>
<tr>
<td>C$_2$H$_5$Cl</td>
<td>0.075</td>
<td>0.016</td>
<td>0.12 ($\text{H}_2^\text{Cl}^+$)</td>
</tr>
<tr>
<td>CH$_3$CF$_3$</td>
<td>0.024</td>
<td>0.0054</td>
<td>0.038 ($\text{H}_2^\text{F}^+$)</td>
</tr>
</tbody>
</table>

$^a$The $\text{H}_3^+$ peak scanned at 2000 V ion accelerating voltage, the $\text{H}_2^+$ peak at 3000 V; each at 70 V nominal ionizing voltage, normal repellers of $\sim$0.01 $V_A$, 0.5 mm collector slit.

$^b$Patterns are expressed as the percent the $\text{H}_3^+$ peak intensity contributes to the total peak intensity.
Table 1. Continued.

- Corrected for contribution of HD$^+$ from the H$_2^+$ peak.
- $D_3^+/D_2^+$ ratio.
- $H_2X^+$ peak intensity as % of total peak intensity.
<table>
<thead>
<tr>
<th>Compound</th>
<th>A.P. (H$_3^+$) (eV)</th>
<th>Standard</th>
<th>Initial K.E. H$_3^+$ (eV)</th>
<th>Relative Yield (Est.)</th>
<th>Method$^a$</th>
<th>$T^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>$25.0\pm1^c$</td>
<td>He$^+$</td>
<td>$&lt;0.7$</td>
<td>$&gt;90%$</td>
<td>NR</td>
<td>$&lt;0.85$</td>
</tr>
<tr>
<td></td>
<td>$(25.3\pm1)^d$</td>
<td></td>
<td>$4.9\pm0.2$</td>
<td>$&lt;10%$</td>
<td>NR</td>
<td>$6.0\pm0.3$</td>
</tr>
<tr>
<td>CD$_4$</td>
<td>$25.5\pm0.5$</td>
<td>$^{22}\text{Ne}^+$</td>
<td>$&lt;0.1$</td>
<td>$&gt;90%$</td>
<td>mss</td>
<td>$&lt;0.14$</td>
</tr>
<tr>
<td></td>
<td>$35.5\pm2^e$</td>
<td></td>
<td>$4.0\pm0.2$</td>
<td>$&lt;10%$</td>
<td>mss</td>
<td>$5.7\pm0.3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;0.5$</td>
<td>$&gt;90%$</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$3.9\pm0.2$</td>
<td>$&lt;10%$</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>$24.6\pm0.5$</td>
<td>He$^+$</td>
<td>$&lt;0.1$</td>
<td>$&lt;10%$</td>
<td>mss</td>
<td>$&lt;0.11$</td>
</tr>
<tr>
<td></td>
<td>$30.0\pm1^e$</td>
<td></td>
<td>$3.8\pm0.1$</td>
<td>$&gt;90%$</td>
<td>mss</td>
<td>$4.2\pm0.1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$4.3\pm0.2$</td>
<td></td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$4.1\pm0.2$</td>
<td></td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>$25.5\pm0.5$</td>
<td>He$^+$</td>
<td>$&lt;0.2$</td>
<td>$&lt;10%$</td>
<td>mss</td>
<td>$&lt;0.21$</td>
</tr>
<tr>
<td></td>
<td>$29.9\pm1^e$</td>
<td></td>
<td>$3.7\pm0.1$</td>
<td>$&gt;90%$</td>
<td>mss</td>
<td>$3.9\pm0.1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$4.1\pm0.2$</td>
<td></td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>$&lt;0.2$</td>
<td></td>
<td>$&gt;80%$</td>
<td></td>
<td>mss</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$3.8\pm0.3$</td>
<td>$&lt;20%$</td>
<td>mss</td>
<td></td>
</tr>
<tr>
<td>C$<em>4$H$</em>{10}$</td>
<td>$26\pm2^c$</td>
<td>He$^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>$22.7\pm1^c$</td>
<td>He$^+$</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>


$^b$Total fragmentation energy, $T$, assuming fragmentation to be $H_3CX^+ \rightarrow H_3^+ + CX$.

$^c$Weak onset over background of HD$^+$ or lower state of low transition probability.

$^d$From reference 1.

$^e$A.P. of high initial kinetic energy state.
Table 3. Comparison of Calculated and Observed Appearance Potentials for the Formation of \( \text{D}_3^+ \) from \( \text{CD}_4 \) and \( \text{H}_3^+ \) from \( \text{C}_2\text{H}_6 \) and \( \text{CH}_3\text{Cl} \).

<table>
<thead>
<tr>
<th>Products</th>
<th>( \text{CD}_4 )</th>
<th>( \text{C}_2\text{H}_6 )</th>
<th>( \text{CH}_3\text{Cl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{D}_3^+ + \text{CD} )</td>
<td>( \text{D}_3^+ + \text{CD} )</td>
<td>( \text{H}_3^+ + \text{C}_2\text{H}_3 )</td>
</tr>
<tr>
<td>(-\Delta H_f(\text{CH}_3X)^b)</td>
<td>0.78</td>
<td>0.78</td>
<td>0.88</td>
</tr>
<tr>
<td>( \Delta H_f(CX) )</td>
<td>6.17</td>
<td>2.82</td>
<td>5.29</td>
</tr>
<tr>
<td>( \Delta H_f(CX^+) )</td>
<td>17.30</td>
<td>11.67(^c)</td>
<td>13.70(^d)</td>
</tr>
<tr>
<td>( \Delta H_f(H_3^+) )</td>
<td>11.12</td>
<td>11.12</td>
<td>11.12</td>
</tr>
<tr>
<td>( \Sigma = \text{Min A.P. at } T=0 )</td>
<td>18.07</td>
<td>29.20</td>
<td>14.82</td>
</tr>
<tr>
<td>( T )</td>
<td>(&lt; 0.2 )</td>
<td>5.7</td>
<td>(&lt; 0.1 )</td>
</tr>
<tr>
<td>( \text{Calc A.P.} )</td>
<td>(&lt; 18.3 )</td>
<td>34.9</td>
<td>(&lt; 14.9 )</td>
</tr>
<tr>
<td>( \text{Obs A.P.} )</td>
<td>25.5±0.5</td>
<td>35.5±2</td>
<td>25.0±0.5</td>
</tr>
<tr>
<td>( \Delta A.P. ) (Obs-Calc)</td>
<td>7.2±0.5</td>
<td>0.6±2</td>
<td>10.1±0.5</td>
</tr>
</tbody>
</table>

\(^a\)Assuming heats of formation of deuterated species equal to those given in Ref. 15 for protonated species.

\(^b\)All heats of formation expressed in eV/molecule.

\(^c\)Assuming \( \Delta H_f(C_2H_3^+) = 269 \text{ Kcal/mole.} \) (Ref. 15).

\(^d\)Assuming \( \Delta H_f(\text{CCl}^+) = 316 \text{ Kcal/mole.} \) Listed values range from 316 to 420 Kcal/mole. (Ref. 15).

\(^e\)Calculated assuming the proton affinity of \( \text{H}_2 \) to be 4.73 eV.
Fig. 1

Peak Sensitivity in Arbitrary Units

Inlet Pressure in \( \mu m \)

- \( \text{CH}_4^+ (\text{CH}_4) \)
- \( \text{H}_2^+ (\text{CH}_4) \)
- \( \text{H}_3^+ (\text{C}_2\text{H}_6) \)
- \( \text{H}_3^+ (\text{CH}_4) \)
- \( \text{D}_3^+ (\text{CD}_4) \)
Fig. 2

Ion Accelerating Voltage in Kilovolts

Peak Intensity in Arbitrary Units

$H_3^+ (CH_4)$

$D_3^+ (CD_4)$

$H_3^+ (C_2H_6)$
Fig. 3

CH$_4^+$ (CH$_4$) and CD$_4^+$ (CD$_4$)
Fraction of Metastable Suppressor Voltage

-29-

22Ne+

D3⁺(CD₄)

D3⁺(CD₄) × 5

Peak Intensity (normalized)

Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9

Electron Energy in eV (approximate scale)

Peak Intensity in Arbitrary Units

A) $D_3^+$ (CD$_4$) 0.970 V$_{mss}$

B) $D_3^+$ (CD$_4$) 0.98535 V$_{mss}$

C) $(I_{D_3^+})^{1/2}$

(Peak Intensity)$^{1/2}$ (curve C)

XBL 708-1935
Fig. 10

Electron Energy in eV (corrected)

Peak Intensity in Arbitrary Units

He$^+$ 0.980 $V_{mss}$

$H_3^+$ ($C_2H_6$) 0.980 $V_{mss}$

$H_3^+$ ($C_2H_6$) 0.9865 $V_{mss}$

$(I_{H_3^+})^{1/2}$

XBL 708-1937
Fig. 11
Fig. 12

Peak Pattern (% of Total Peak Intensity)

H$_2^+$ (n-alkanes)

H$_3^+$ (n-alkanes)

H$_3^+$ (1-alkenes)

Carbon Number
Fig. 13
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