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## EXCESS-KINETIC-ENERGY IONS IN ORGANIC MASS SPECTRA

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## ABSTRACT

The characteristics of excess-kinetic-energy ions in mass spectra have been studied with a Dempster type mass spectrometer. A method was devised whereby the total initial kinetic energies possessed by such ions could be measured more accurately than has been done previously, and the kinetic energies of methyl ions, both near-thermal and excess-kinetic-energy, from a wide variety of different organic compounds are presented. Appearance potential curves were obtained for several excess-kinetic-energy methyl ions; these show a second power dependence of cross-section on electron energy in the threshold region with threshold values of the order of 30 eV. Finally, a method of estimating the discrimination factor of the mass spectrometer toward ions possessing excess kinetic energy was utilized to obtain values for the actual abundances of excess-kinetic-energy methyl ions in the fragmentations of several organic compounds. Actual abundances of from 2 to 10% of the total ions in the mass spectrum were found from many compounds.

The values of appearance potentials, kinetic energies, and abundances that have been measured for the complementary excess-kinetic-energy ion pairs from methyl amine (masses 15 and 16) and propane (masses 15 and 27) are consistent with a mechanism for formation in which both ions arise from the same initial state in each respective case. The data support the suggestion that excess-kinetic-energy fragment ions from the organic compounds are formed by breakdown of doubly charged parent ions.

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## INTRODUCTION

Ions with excess kinetic energy have long been known to exist in the mass spectra of molecules. In his 1930 study of the hydrogen molecule mass spectrum, Bleakney found that $H^+$ ions of about 4.5 eV kinetic energy appeared, in addition to the thermal $H^+$ ions.[1] When mass spectrographic work was extended to polyatomic species, it was found that ions of excess kinetic energy also appeared in their mass spectra. Thus, Hustrulid, Kusch, and Tate found excess-kinetic-energy ions of masses 12 to 15 and 25 to 27, corresponding to various $C_1$ and $C_2$ fragment ions in the mass spectrum of benzene.[2] Whereas Bleakney had determined that the excess-kinetic-energy ions from $H_2$ arose from excitation to the repulsive $^2\Sigma_u^+$ state of the hydrogen molecule ion followed by dissociation, Hustrulid, Kusch and Tate tentatively ascribed the excess-kinetic-energy ions occurring in the benzene spectrum to the dissociation of doubly charged ions into two singly charged smaller fragments.

Mohler, Dibeler, and Reese investigated the excess-kinetic-energy methyl ions appearing in the mass spectra of several hydrocarbons and interpreted their data in terms of the doubly charged ion mechanism.[3] Later Stanton reinvestigated the propane mass spectrum and reached the conclusion that the excess-kinetic-energy methyl ions arising from propane could not

be explained by a simple doubly charged-ion fragmentation process.[4] Recently, Tsuchiya made more extensive studies of the excess-kinetic-energy ions in the propane spectrum and deduced from his data that the excess-kinetic-energy fragment ions could be explained on the basis of multiple fragmentations of the doubly charged propane molecule ion.[5] Bracher, Ehrhardt, Fuchs, Osberghaus, and Taubert, in a paper concerned mainly with the kinetic energy distributions of quasi-thermal ions, have also considered the source of excess-kinetic-energy ions in the propane mass spectrum.[6] They concluded that although the energies of fragment ions were approximately correct to fit the doubly charged ion picture, in the absence of further data the question must remain unresolved.

## INSTRUMENTATION

All data obtained in this research were taken on a Consolidated Electrodynamics Corporation model 21-103A mass spectrometer. This instrument was modified in the following ways to increase its flexibility: a bucking battery was installed in the grid potential control of the 100TH tube in the voltage selector circuit to permit reduction of the accelerating voltage to as low as 75 volts. A 10-turn, 100-ohm Helipot was inserted between the accelerating voltage divider circuit and ground for a fine control on the voltage selector circuit. A Leeds and Northrup type B potentiometer was used to permit measurement of the accelerating voltage with a precision of $\pm$ 0.01 V. The logarithmic potentiometer controlling the metastable suppressor voltage was replaced with a linear Helipot and a fixed resistor which permitted the metastable suppressor voltage to be set reproducibly to $\pm$ 0.01 V with respect to the accelerating voltage at any voltage within its normal range. The voltage range of the repellers was increased to

-22-1/2 V to +80 V by inserting a pair of potentiometers operated in tandem on either side of the divider circuit controlling the repeller voltages and by placing dry cell batteries in the network supplying voltage to the repellers. The use of tandem potentiometers above and below the repeller network allowed continuous adjustment of the repeller without changing the metastable suppressor level. A battery operated vacuum tube voltmeter, floated at high voltage, measured the metastable suppressor and repeller voltages accurately while the machine was in operation. A Leeds and Northrup potentiometer that floated at high voltage was used to set and measure the nominal ionizing voltage to $\pm$ 0.05 V. A bucking battery installed between the anode and block enabled the anode voltage to be reduced to +5 V with respect to the block. Finally, a charging condenser and switch installed in the magnet current control circuit allowed the magnetic field to be varied in a uniform manner to scan magnetically a short range of M/q values.

The normal operating conditions of this instrument are the following: magnetic field set so the product of mass and accelerating voltage (MV) equals 45,000, repeller voltages set at approximately 1% of the accelerating voltage (inner repeller slightly higher in potential than outer -- exact setting determined by optimum focus conditions), metastable suppressor grounded to analyzer, nominal ionizing voltage = 70 V, and ionizing current = 37.5 $\mu$ a.

## PROCEDURE AND DATA

### Kinetic Energies

The kinetic energy possessed by excess-kinetic-energy ions has previously been measured by determining the difference in accelerating

voltage necessary to focus thermal and excess-kinetic-energy ions of a given mass at constant magnetic field.[3] This method measures accurately the difference in kinetic energy between ions in the "thermal" peak and those in the excess-kinetic-energy peak; however, it does not by itself comprise an adequate measure of the actual kinetic energy of the excess energy ions. To obtain that quantity, one must also know the amount of excess kinetic energy possessed by the "thermal" ions. This point was not considered by previous workers.[3,7]

To obtain measurements of both the excess energy of the "thermal" ions and that of the high-energy ions, the following procedure was devised. The magnetic field of the mass spectrometer was set at some constant value (typically, a magnetic field strength at which ions of $MV/q = 3250$ were focused), monitored by a bismuth wire fluxmeter,[8] and maintained constant to within 0.02 gauss by manual adjustment during the course of the measurements. Initially, a reference mixture of methane and neon was admitted to the ion source and the accelerating voltages required to focus the $M/q = 15$ and $M/q = 20$ ion peaks were measured. Then, after pumpout of the system, an organic compound of interest was admitted to the ion source, again in the presence of neon, and the focus voltages for the $M/q = 15$, $M/q = 15^*$ (excess-kinetic-energy component), and $M/q = 20$ peaks were measured. Under such conditions, the shift observed in the $M/q = 20$ focus voltage ($\Delta V_{20}$) represents the influence of contact potentials on the voltages; the shift in the focus voltage ($\Delta V_{15}$) for the $M/q = 15$ peak represents the excess kinetic energy of the "thermal" peak plus the influence of contact potentials; and the actual kinetic energy for the excess-kinetic-energy ions is given by the expression

$$T_i = V_{15} - V_{15}^* + \Delta V_{15} - \Delta V_{20} \qquad (1)$$

Repeated measurements of kinetic energies for some of the compounds studied indicated that the reproducibility of focus voltage measurements was ± 0.01 V; furthermore, measurement of energies by a complementary method, a modification of a technique developed by Kandel for the determination of metastable suppressor cutoff curves,[9] gave identical values for kinetic energies within the limits of reproducibility (± 0.05 V). Since three separate voltage measurements were involved in the determination of each kinetic energy, the probable error of the energy measurements was ± 0.02 V.

Values obtained for the kinetic energies of thermal and high-energy M/q = 15 ions from a wide variety of organic compounds are given in Table I. These values cannot be compared directly with those obtained by other workers, who did not determine the kinetic energies of "thermal" ions; however, the kinetic energy differences between thermal and excess-kinetic-energy ions measured in this work are in general agreement with previous measurements.[3,7]

Kinetic energies were measured for two ions of M/q ratio different from 15, the $NH_2^+$ ion from methyl amine and the $C_2H_3^+$ ion from propane. The foregoing method was not used for the determination of these energies; rather, they were determined by use of the metastable-suppressor cutoff curves for the ion peaks (see fig. 1).[9] Rather than use the actual disappearance voltage for the peak as was done by Kandel previously, it was necessary to determine an average disappearance voltage, since the energy of interest was not the maximum kinetic energy of the ions but the most probable energy. By comparison with kinetic energies of M/q = 15 ions obtained by accelerating voltage measurements, it was determined that the midpoint of the region of linear decrease of the peak height with metastable-suppressor voltage corresponded to the average disappearance voltage.

To obtain the actual cutoff voltage, the applied voltage must be multiplied by 0.971, a factor determined empirically from thermal ion cutoff curves, to correct for the fact that the voltage actually experienced by the ions is somewhat less than that applied to the metastable suppressor.[10]

In order to insure that the difference in energy between the complementary ions was measured accurately, metastable-suppressor cutoff curves were run for both ions and the midpoint was then determined in the same manner for each, by normalizing the two cutoff curves at an intermediate metastable suppressor voltage before locating the midpoints. Owing to the difficulty of determination of midpoints and to possible interference from low kinetic energy ions, the probable error of such kinetic energy measurements is $\pm$ 0.05 V; however, the probable error of the kinetic energy difference between complementary ions is somewhat less than this, $\pm$ 0.02 V, since the major source of error, arising from the difficulty of determining the midpoint, is eliminated by choosing the midpoint in the same manner for each ion.

The values obtained by these measurements are 2.38 V for the mass 16 ($NH_2^+$) excess-kinetic-energy ions from methyl amine and 1.18 V for the mass 27 ($C_2H_3^+$) excess-kinetic-energy ions from propane.

Appearance Potentials

The variation of peak height with electron energy for excess-kinetic-energy ions was observed to obey a second power law for 6 to 8 volts above the threshold; it was therefore possible to make a linear extrapolation of a square root plot of peak height against electron energy to give an energy-axis intercept (Fig. 2).

Relative appearance potentials were determined for the excess-kinetic-energy ion pairs $CH_3^+$ and $C_2H_3^+$ from propane and $CH_3^+$ and $NH_2^+$ from methyl amine by direct comparison of such square root plots under conditions where the thermal ion peak was virtually eliminated (the inner repeller was set at a slightly negative voltage and the outer repeller grounded to the Isatron. Under these conditions thermal ions are prevented from leaving the accelerating region, whereas excess-kinetic-energy ions are affected hardly at all). Such comparisons showed the appearance potentials under these conditions to be the same, within the experimental error of ± 0.1 V, for the two members of each pair. As calibrating gases cannot be run under these conditions, measurements at negative repeller voltages cannot be used to determine absolute values of appearance potentials.

Absolute appearance potentials were obtained for excess-kinetic-energy ions from several organic compounds by comparison of the energy-axis intercept for the high energy ion with that for a rare gas ion, usually $Ne^+$, introduced into the ion source simultaneously with the organic compound of interest. Repellers were set slightly positive and the anode was set at +5 volts. A similar determination was carried out on the rare gas ions $Ne^+$, $He^+$, and $Kr^{++}$ from a mixture of the three rare gases, and the values obtained for the differences in appearance potentials among these ions agreed within ± 0.05 V with the differences in spectroscopic values. Since extrapolated energy axis intercepts could not be determined as accurately for excess-kinetic-energy ions as for rare gas ions, owing to a slight interference from thermal ions of the same mass as the excess-kinetic-energy ions being measured, values determined for those ions are estimated to be accurate only to ± 0.2 V. Appearance potential values are given in Table II.

Relative Abundances

The determination of relative abundances of ions of excess kinetic energy in a given ion peak depends on several experimental factors. Firstly, it is necessary that the peak be completely separated into thermal and excess-kinetic-energy components over some range of values of the ion-accelerating voltage. This separation is accomplished at low accelerating voltages. Secondly, one must know how the peak height of a thermal peak varies as the accelerating voltage is increased. This variation was measured for the methyl ion peaks from several compounds which were known to have very little or no excess-kinetic-energy methyl ion components. The curves obtained for methane, methanol, and methyl chloride are shown in Fig. 3. These curves show slightly different characteristics owing to the different, though small, initial kinetic energies of the "thermal" ions from the three compounds.

Finally, one must measure the variation of methyl-ion peak height with accelerating voltage for a compound known to possess both "thermal" ions and excess-kinetic-energy ions. From this variation the relative abundances of thermal and excess-kinetic-energy methyl ions under normal mass spectrometer operating conditions can be determined in the following manner.

First, it is assumed that the variation of peak height with accelerating voltage is a function of the initial kinetic energy and mass of the ions comprising the peak but independent of the compound from which they are derived. In that case, the variation of the peak height of the thermal component of the total ion peak is easily determined. The curve in Fig. 3 corresponding to ions of the same kinetic energy as the "thermal"

ions of the compound being analyzed is selected. This curve is normalized to fit the thermal-ion peak heights measured at low accelerating voltages, and the normalized curve then gives the thermal-ion peak height at higher accelerating voltages.

Next, it is assumed that the total measured peak height at high accelerating voltages is simply the sum of contributions from thermal and excess-kinetic-energy ions. Then, the excess-kinetic-energy ion peak height at any accelerating voltage is just the difference between the total measured peak height and the normalized thermal ion curve height.

This method of determination is illustrated in Table III, where it has been carried out for the methyl ion peak from propane. Column I shows the accelerating voltages; columns II, III, and IV the measured peak heights, resolved at low accelerating voltages and total at high accelerating voltages; column V gives the thermal-ion peak height obtained by normalizing the peak height curve given for methanol in Fig. 3 to fit the measured thermal-ion peak height at 200-V accelerating voltage; and column VI shows the excess-kinetic-energy peak height, obtained by subtraction of column V from column III.

The excess-kinetic-energy peak height for the methyl ion from propane is plotted in Fig. 4 as a function of accelerating voltage. Below 500-V, measured peak heights are used; above 500-V, computed peak heights. The accuracy of the method of analysis can be estimated by comparing Fig. 4 to Fig. 5, curve B, wherein the measured methyl ion peak height is plotted against accelerating voltage for benzene. The $M/q = 15$ peak from benzene is almost exclusively an excess-kinetic-energy peak; thus the curve B in Fig. 5 gives the typical behavior with accelerating voltage of an excess-kinetic-energy ion peak.

The two figures agree perfectly with the exception of points in the 0.8 kV region, where points in the propane curve are low. Such a discrepancy is expected, because the assumption of additivity of the thermal and excess-kinetic-energy ion peaks is not valid in that accelerating voltage region, owing to incomplete superposition of the peaks.

The relative abundances of thermal and excess-kinetic-energy ions observed under normal mass spectrometer operating conditions are given in Table IV for several different organic compounds. These abundances are listed in the form of percentages, out of all the ions observed in the mass spectra, that ions of a given type constitute.

Absolute Abundances

Assessment of the absolute abundances of excess-kinetic-energy ions is dependent on a knowledge of the amount of discrimination of the mass spectrometer slit system against high kinetic energy ions. Berry has derived expressions from which the discrimination effects in the accelerating and analyzing regions of the mass spectrometer can be computed.[11] Coggeshall showed that in the presence of an electric field only there is no discrimination within the ion source[12] and that in the presence of a magnetic field there is little discrimination if the electric field is moderately strong.[13] Since the repeller field was at least moderately strong throughout the experiments used to determine abundances, the equations derived by Berry have been applied without further correction for ion source exit slit discrimination.

Assuming a Maxwellian distribution of energies of the ions, Berry gives for the collection efficiency, N, the equation:

$$N = 1/2(k+1)\mathrm{erf}\,[(k+1)\sigma] - 1/2\,|k-1|\,\mathrm{erf}[(k-1)\sigma] + (2\pi^{1/2}\sigma)^{-1}$$

$$\{\exp[-(k+1)^2\sigma^2] - \exp[-(k-1)^2\sigma^2]\} \qquad (2)$$

The symbols used in the above Equation are defined for two different regions: region (1), the accelerating region between the exit slit of the Isatron and the accelerating slit; and region (2), the analyzer region between the accelerating slit and the collector slit. $N_1$ is defined as the ratio of the number of ions of a given mass that pass through the accelerating slit to the number of ions of the same mass that are formed in an area of the electron beam equal to the area of the exit slit of the Isatron. $N_2$ is defined as the ratio of the number of ions of a given mass that pass through the collector slit to the number of ions of the same mass that pass through the accelerating slit.

The k's are given by the expression

$$k_1 = w_e/w_1 \; ; \qquad k_2 = l_2/l_1 \qquad (3)$$

where $w_e$ is the half width of the Isatron slit, $w_1$ and $l_1$ the half width and half length of the accelerating slit, and $l_2$ the half length of the collector slit. The parameter $\sigma$ is given by the expressions:

$$\sigma_1 = 1/2(V/T_i)^{1/2} w_1/L_1 ; \qquad \sigma_2 = (V/T_i)^{1/2} l_2/L_2, \qquad (4)$$

where $L_1$ and $L_2$ are the distances traveled by the ions in the regions (1) and (2), respectively; V is the accelerating voltage; and $T_i$ is the initial kinetic energy of the ions.

Berry found better agreement of the theory with his experimental data if he used for the parameters $k_1$ and $k_2$ "effective" values that differed somewhat from the true ratios of slit dimensions. Accordingly, we carried

out calculations for various values of $k_1$ and $k_2$ and compared the results with the experimental variations with accelerating voltage of peak heights of methyl ions possessing various initial kinetic energies. Such comparison of theory and experiment for the values of $k_1$ and $k_2$ that gave the best fit, 3.0 and 2.0, is shown in Fig. 6. The values used for other quantities appearing in the equation are shown in Table V.

The k-values giving the best fit are quite reasonable. For the analyzing region the best value for k ($k_2 = 2.0$) is equal to the geometric value, as is to be expected since in that region the electric and magnetic field characteristics are quite close to those that Berry assumed in deriving the collection efficiency equation. In the accelerating region, on the other hand, the best value for k ($k_1 = 3.0$) is quite different than the geometric value (1.0), reflecting collection characteristics in that region that are considerably better than those predicted by the unadjusted theory. This is again to be expected, since the field characteristics in the accelerating region are greatly perturbed from the ideal conditions considered by Berry, owing to the presence in the accelerating region of a pair of focus electrodes that serve to improve the collection efficiency of the spectrometer.

In the last column of Table IV the actual percentages of excess-kinetic-energy ions are given, as calculated from the observed percentages by means of Eq. 2. In Fig. 7 the actual percentages of methyl ions from normal hydrocarbons are compared with observed values. In view of the degree of success with which the calculated collection efficiency curves match the experimental curves and the relative insensitivity of collection efficiencies for excess-kinetic-energy ions to the value of k used (variation of 0.2 in $k_1$ results in only a 5% change in the calculated collection

efficiency, although such a variation results in a much poorer overall fit to the observed efficiency curves), we estimate the probable error of the calculated actual methyl ion percentages to be about ± 10%. Comparison of the data for propane with approximate ratios of thermal ion abundance to excess-kinetic-energy ion abundance computed from data obtained by Bracher, Ehrhardt, Fuchs, Osberghaus, and Taubert by another technique shows qualitative agreement.[6]

## DISCUSSION

The data presented in this paper are, in the main, consistent with the doubly charged ion mechansim for formation of excess-kinetic-energy ions. For both methyl chloride and methyl amine, excess-kinetic-energy ions of the mass complementary to that of methyl ions are observed, and for propane, although the ethyl ion is not observed to possess a measurable excess-kinetic-energy ion component, excess-kinetic-energy ions at other $C_2$ masses are observed. Moreover, a calculation of the absolute abundances of methyl and amino excess-kinetic-energy ions from methyl amine indicates that equal numbers of these ions are formed by impact of 70-V electrons. A qualitative survey of several other methyl compounds shows that when excess-kinetic-energy methyl ions appear in the mass spectrum, the complementary excess-kinetic-energy ions also appear. In the only case for which no excess-kinetic-energy methyl ions are observed, that of methyl fluoride, the complementary excess-kinetic-energy $F^+$ ions are also absent from the spectrum (both the methyl and fluoride ion peaks from methyl fluoride are quasi-thermal, possessing about 0.5 V kinetic energy).

Stronger evidence in favor of the doubly-charged ion mechanism is afforded by comparative appearance potential measurements for the methyl and amino excess-kinetic-energy ions from methyl amine and the methyl and vinyl excess-kinetic-energy ions from propane. The appearance potentials of these complementary ion pairs are the same within experimental error, indicating that both ions arise from the same energy state, presumably one of a doubly charged ion. Furthermore, the appearance potential curves for all excess-kinetic-energy ions for which measurements were made show a second power variation with electron energy of cross-section for ion formation in the threshold region, as is predicted by theory for double ionization processes.[14] The latter behavior is not, however, conclusive proof that the mechanism of formation of excess-kinetic-energy ions involves double ionization as is demonstrated by the appearance potential curve for excess-kinetic-energy $D^+$ ions from $D_2$. This curve, too, shows a second power dependence of cross-section on electron energy near threshold, but in this case the excess-kinetic-energy ions are known to be formed from the excited singly-charged $^2\Sigma_u^+$ state of the molecule ion.[1]

The magnitudes of appearance potentials for excess-kinetic-energy methyl ions are also in the range that one expects for doubly charged ions. One is hard pressed to explain appearance potentials in the range observed, 28-32 V, by a singly charged ion mechanism, since one is forced to postulate excess excitation energy in the fragments in the amount of 10 to 12 volts, considerably more than enough to induce further fragmentations. On the other hand, if one assumes that in the higher hydrocarbons as in propane the heavier mass fragment breaks down further by eliminating a hydrogen molecule, then the appearance potentials that one calculates using tabulated

appearance potentials for thermal fragment ions,[15] the ionization potential of the methyl radical (9.82 V),[16] and the minimum possible kinetic energy of the fragments, agree reasonably with the measured values, as is shown in Table VI. In all hydrocarbon cases the measured value is somewhat higher than the calculated value, indicating either that some excitation is present in the fragments even at threshold or that the $H_2$ molecule is eliminated with some kinetic energy.

Perhaps the strongest evidence favoring the doubly-charged ion mechanism is provided by comparison of the kinetic energies of the complementary ions. According to the law of conservation of momentum, if the two ions are formed in the same process, their kinetic energies must be partitioned inversely as the ratios of the ion masses. For methyl amine this requires that the kinetic energies of the methyl and amino ions be in the ratio of 1.067. The measured value is $1.075 \pm 0.020$.

For propane the agreement is not as good: assuming that the $H_2$ molecule is eliminated after cleavage of the carbon-carbon bond, the measured ratio of kinetic energies of mass 15 to mass 27 ions is $2.24 \pm 0.1$, compared to the required ratio of 2.08. However, the low magnitude of excess kinetic energy of the mass 27 ions coupled with the extremely high abundance of quasi-thermal ions of that mass makes it quite likely that in the determination of the kinetic energy of the mass 27 ions there was some interference from the higher energy portion of the quasi-thermal distribution. The effect of such interference would be to shift the measured kinetic energy of the excess-kinetic-energy vinyl ions downward from the true value. Such an interference can account for the high kinetic energy ratio obtained in the measurement.

Within the limits of error of the measurements, the data obtained in this research are consistent with the suggestion of Hustrulid, Kusch, and Tate that excess-kinetic-energy organic fragment ions arise from dissociation of doubly charged ions.[2] Of all the organic compounds for which measurements were made, for only two, methyl amine and propane, could an adequate test of the mechanism be made. Even in the case of these particular compounds it is not possible to rule out completely the possibility that singly charged repulsive ion states contribute in the formation of excess-kinetic-energy ions, but it appears unlikely that the contribution of such states can be significant.[17]

The figures given in Table IV indicate that from many compounds, a significant proportion (up to 10%) of the total ions formed under bombardment by 70-V electrons are ions possessing excess-kinetic-energy. This proportion is high enough, we believe, that the states that give rise to these ions must be included in the breakdown scheme of any comprehensive theory of mass spectra based on impact with 70 volt electrons. As shown in Table I, the occurrence of high-kinetic-energy ions is a general phenomena, hence must be considered for all types of compounds.

From the point of view of applications of mass spectra to chemical systems undergoing reactions, the abundances of excess-kinetic-energy ions measured in this work may have considerable importance. Recent work of Giese and Maier has shown that ion kinetic energy can be quite effective in inducing endothermic chemical reactions.[18] In view of this, the possibility must be considered that excess-kinetic-energy ions play a significant role in the chemical transformation of organic species under the influence

of ionizing radiation. Endothermic reactions induced by ions with kinetic energy may play a secondary but still significant role in such transformations.

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## FIGURE CAPTIONS

Figure 1. Variation of peak heights with metastable-suppressor voltage. Data taken at 0-V repellers and 300-V accelerating voltage. A: Curve for thermal M/q = 20 peak from neon; B: Curve for 2.66-eV excess-kinetic-energy M/q = 15 peak from isobutane.

Figure 2. Ionization efficiency curves for $Kr^{++}$ and excess-kinetic-energy $CH_3^+$ ions from a krypton-benzene mixture.

Figure 3. Variation with accelerating voltage of peak heights for near-thermal ions of M/q = 15. Data taken with repeller voltage at 1% of accelerating voltage. A: Curve for thermal ions (methane); B: Curve for 0.15-eV ions (methanol); C: Curve for 0.25-eV ions (methyl chloride).

Figure 4. Computed variation with accelerating voltage of peak height of excess-kinetic-energy M/q = 15 ion peak from propane.

Figure 5. Variation of peak heights with accelerating voltage. Data taken with repeller voltage at 1% of accelerating voltage. A: Curve for thermal M/q = 15 peak from methane; B: Curve for 2.27-eV excess-kinetic-energy M/q = 15 peak from benzene.

Figure 6. Comparison of theory with experiment: discrimination of the mass spectrometer against methyl ions of different kinetic energies (in eV), as a function of the accelerating voltage. Points are experimental; smooth curves are theoretical. The source compound for the methyl ions and the kinetic energies of the ions, are as follows: o - $CH_4$ (thermal); ● - $CH_3OH$ (0.14 eV); □ - $CH_3Cl$ (0.27 eV); ■ - $CH_3F$ (0.58 eV); Δ - $C_6H_6$ (2.27 eV).

Figure 7. Comparison, for normal aliphatic hydrocarbons, of observed percentage of methyl ions in mass spectra with actual percentage formed by electron impact (for 70-V electrons).

Table I. Kinetic Energies of M/q = 15 Fragment Ions

| Compound | K.E. of Thermal M/q = 15 ion | K.E. of excess K. E. M/q = 15 ion |
|---|---|---|
| | A. Paraffins | |
| ethane | 0.06 | 2.45 |
| propane | 0.15 | 2.65 |
| n-butane | 0.20 | 2.48 |
| isobutane | 0.20 | 2.66 |
| n-pentane | 0.17 | 2.24 |
| neopentane | 0.20 | 2.71 |
| n-hexane | 0.23 | 1.95 |
| di-isopropyl | 0.17 | 2.50 |
| n-heptane | 0.17 | 1.83 |
| 2,4-dimethyl pentane | 0.23 | 2.08 |
| 2,5-dimethyl hexane | 0.19 | 2.06 |
| | B. Olefins | |
| propylene | 0.08 | 2.75 |
| butene-1 | 0.15 | 2.59 |
| cis-butene-2 | 0.15 | 2.65 |
| isobutylene | 0.12 | 2.76 |
| pentene-1 | 0.13 | 2.30 |
| 3-methyl butene-1 | 0.17 | 2.52 |
| hexene-1 | 0.11 | 2.02 |
| 4-methyl pentene-1 | 0.16 | 2.21 |
| heptene-1 | 0.16 | 1.85[a] |

Table I. (Cont.)

| Compound | K.E. of Thermal M/q = 15 ion | K.E. of excess K.E. M/q = 15 ion |
|---|---|---|
| | C. Dienes | |
| 1,2-butadiene | 0.14 | 2.61 |
| 1,3-butadiene | 0.12 | 2.59 |
| 2-methyl butadiene-1,3 | 0.20 | 2.60 |
| 2,3-dimethyl butadiene-1,3 | 0.09 | 2.48 |
| 1,5-hexadiene | 0.16 | 2.20 |
| 2,5-dimethyl hexadiene-1,5 | 0.17 | 2.09 |
| | D. Alcohols | |
| ethanol | 0.12 | 2.96 |
| n-propanol | 0.16 | 2.71 |
| isopropyl alcohol | 0.16 | 2.83 |
| n-butyl alcohol | 0.13 | 2.28 |
| isobutyl alcohol | 0.16 | 2.76 |
| t-butyl alcohol | 0.18 | 2.82 |
| n-amyl alcohol | 0.25 | 1.75[a] |
| isoamyl alcohol | 0.22 | 2.40 |
| neopentyl alcohol | 0.24 | 2.80 |
| 1,2-propane diol | 0.04 | 2.7[a] |

Table I. (Cont.)

| Compound | K.E. of Thermal M/q = 15 ion | K.E. of excess K. E. M/q = 15 ion |
|---|---|---|
| | E. Aromatic Compounds | |
| benzene | 0.14 | 2.27 |
| chlorobenzene | (b) | 2.35 |
| aniline | 0.06 | 2.01 |
| toluene | 0.20 | 2.32 |
| ethyl benzene | 0.23 | 2.26 |
| n-propyl benzene | 0.28 | 2.11 |
| | F. Halides | |
| methyl chloride | 0.27 | 4.15 |
| ethyl chloride | 0.21 | 3.02 |
| n-propyl chloride | 0.20 | 2.85 |
| isopropyl chloride | 0.22 | 2.95 |
| n-butyl chloride | 0.21 | 2.50 |
| isobutyl chloride | 0.21 | 2.78 |
| t-butyl chloride | 0.26 | 2.89 |
| n-amyl chloride | 0.16 | 2.26 |
| isoamyl chloride | 0.17 | 2.54 |
| n-heptyl chloride | 0.22 | 1.79 |
| ethyl bromide | 0.21 | 3.31 |
| n-propyl bromide | 0.21 | 2.94 |
| n-butyl bromide | 0.21 | 2.48 |
| n-butyl iodide | 0.23 | 2.27 |
| 1,1-dichloroethane | 0.27 | 3.51 |

Table I. (Cont.)

| Compound | K.E. of Thermal M/q = 15 ion | K.E. of excess K.E. M/q = 15 ion |
|---|---|---|
| 1,1-dichloropropane | 0.21 | 2.90 |
| 1,2-dichloropropane | 0.21 | 3.08 |
| 2,2-dichloropropane | 0.20 | 3.23 |
| 1,1-dichlorobutane | 0.26 | 2.54 |
| 1,1,1-trichloroethane | 0.24 | 3.25 |
| 1,1,1,2-tetrachloropropane | 0.23 | 3.10 |
| 1-chloropropene-1 | 0.16 | 2.8[a] |
| 3-chloro-2-methylpropene-1 | 0.12 | 2.76 |
| 1,1-dichloropropene-1 | 0.21 | 3.11 |
| G. Cyclic Compounds | | |
| methyl cyclopropane | 0.20 | 2.65 |
| cyclopentane | 0.15 | 2.53 |
| cyclopentene | 0.25 | 2.54 |
| cyclopentanone | 0.20 | 2.49 |
| cyclopentanol | 0.25 | 2.23 |
| cyclopentyl chloride | 0.13 | 2.35 |
| methyl cyclopentane | 0.22 | 2.30 |
| cyclohexane | 0.12 | 2.26 |
| cyclohexene | 0.17 | 2.37 |
| cyclohexyl bromide | 0.20 | 2.23 |
| methyl cyclohexane | 0.12 | 2.16 |
| cyclooctatetraene | (b) | 2.21 |

Table I. (Cont.)

| Compound | K.E. of Thermal M/q = 15 ion | K.E. of excess K.E. M/q = 15 ion |
|---|---|---|
| H. Miscellaneous Compounds | | |
| methyl acetylene | 0.02 | 2.47 |
| acetone | 0.12 | 3.41 |
| di-n-propyl ketone | 0.18 | (c) |
| propionaldehyde | 0.11 | 2.97 |
| n-butyraldehyde | 0.15 | 2.35[a] |
| propionic acid | 0.10 | 2.95 |
| n-butyric acid | 0.16 | 2.48 |
| n-propyl formate | 0.23 | 2.25[a] |
| di-n-propyl ether | 0.18 | (c) |
| n-propyl carbonate | 0.25 | (c) |
| methyl amine | 0.09 | 2.56 |
| ethyl amine | 0.01 | 2.67 |
| n-propyl amine | 0.10 | 2.39 |
| di-n-propyl amine | 0.20 | 2.26 |
| tri-n-propyl amine | 0.19 | 2.10 |
| n-butyronitrile | 0.17 | 2.65 |
| n-propyl mercaptan | 0.16 | 2.49 |

[a] Resolution of excess K.E. peak poor - value imprecise.

[b] Height of thermal peak insufficient to permit determination of K. E.

[c] Excess K.E. peak present but not sufficiently resolved to permit determination of K.E.

Table II. Appearance Potentials of Excess-Kinetic-Energy Ions

| Compound | Ion | A.P. | Reference Ion |
|---|---|---|---|
| benzene | $CH_3^+$ | 28.2 ± 0.2 | (a) |
| ethane | $CH_3^+$ | 30.3 | $Ne^+$ |
| propane | $CH_3^+$ | 30.8 | $Ne^+$ |
| propane | $C_2H_3^+$ | 30.8 | (b) |
| n-butane | $CH_3^+$ | 29.7 | $Ne^+$ |
| isobutane | $CH_3^+$ | 29.4 | $Ne^+$ |
| n-pentane | $C_2H_5^+$ | 28.1 | $Ne^+$ |
| neopentane | $CH_3^+$ | 29.5 | $Ne^+$ |
| n-heptane | $CH_3^+$ | 27.9 | $Ne^+$ |
| n-heptane | $C_2H_5^+$ | 24.3 | $Ne^+$ |
| isopropyl chloride | $CH_3^+$ | 29.7 | $Ne^+$ |
| isopropyl alcohol | $CH_3^+$ | 30.2 | $Ne^+$ |
| benzene | $C_2H_3^+$ | 31.1 | $Ne^+$ |
| benzene | $C_2H_2^+$ | 32.6 | $Ne^+$ |
| deuterium | $D^+$ | 25.3 | (c) |

[a]Value represents the average of four separate determinations using both $Ne^+$ and $Kr^{++}$ as reference ions.

[b]Excess kinetic energy $CH_3^+$ ion from propane used as a reference.

[c]Value obtained from two separate determinations, one using the thermal $D^+$ ions from $D_2$, the other the $CH_3^+$ ions from benzene, as references.

Table III. Breakdown of Total Peak into its Components for Propane M/q = 15 Ion Peak

| I | II | III | IV | V | VI |
|---|---|---|---|---|---|
| Accelerating voltage | Peak ht. thermal (meas.) | Sum. Pk. height (meas.) | Excess K.E. pk. ht. (meas.) | Computed thermal pk. ht.(a) | Computed excess K.E. pk. height(b) |
| 78 | 77.7 | -- (c) | 4.4 | 79.1 | -- |
| 115 | 142.8 | -- | 10.5 | 149.7 | -- |
| 145 | 193.2 | -- | 16.8 | 195.7 | -- |
| 195 | 264 | -- | 29.9 | 264 (d) | -- |
| 300 | 396 | -- | 67.4 | 375.7 | -- |
| 400 | 470 (e) | -- | 111.6 (f) | 452 | -- |
| 500 | 546 (e) | -- | 157.8 (f) | 516 | -- |
| 600 | --- (g) | 684 (h) | --- (g) | 565 | 119 (h) |
| 900 | --- | 976 (h) | --- | 656 | 320 (h) |
| 1210 | --- | 1182 | --- | 708 | 474 |
| 1410 | --- | 1314 | --- | 734 | 580 |
| 1810 | --- | 1533 | --- | 769 | 764 |
| 2010 | --- | 1632 | --- | 777 | 855 |
| 2515 | --- | 1872 | --- | 793 | 1079 |
| 3035 | --- | 2103 | --- | 803 | 1300 |
| 3480 | --- | 2280 | --- | 809 | 1471 |
| 3615 | --- | 2316 | --- | 809 | 1507 |

(a) Obtained from measured variation of peak height with accelerating voltage for methanol M/q = 15 ion (0.15 eV K.E.) by normalization.

(b) Obtained by subtraction of Column V from Column III.

(c) Sum of peak heights not measured when thermal and excess energy peaks were resolved.

Table III. (Cont.)

(d) Methanol peak height variation curve normalized to propane thermal peak height at this accelerating voltage.

(e) Measured peak height somewhat too high because of partial addition of the excess K.E. peak.

(f) Measured peak height somewhat too high because of partial addition of thermal peak.

(g) Individual peak heights not measurable since two peaks were merged.

(h) Somewhat too low because of incomplete addition of peak heights.

Table IV. Percentages of fragment ions of certain masses relative to total ions observed in mass spectra.

| Compound | M/q | Thermal ion percentage | Observed excess K.E. ion percentage | Actual excess K.E. ion percentage (calculated)[a] |
|---|---|---|---|---|
| ethane | 15 | 1.54 | 1.13 | 3.34 |
| propane | 15 | 1.10 | 1.79 | 5.42 |
| n-butane | 15 | 0.95 | 1.88 | 5.94 |
| isobutane | 15 | 1.41 | 2.39 | 7.99 |
| n-pentane | 15 | 0.77 | 1.30 | 4.47 |
| neopentane | 15 | 0.97 | 3.17 | 10.79 |
| n-heptane | 15 | 0.51 | 0.74 | 1.94 |
| 2,4-dimethyl pentane | 15 | 0.63 | 1.95 | 5.45 |
| n-decane | 15 | 0.22 | 0.36 | 0.93 |
| benzene | 15 | $<0.1$ | 0.65 | 1.98 |
| p-xylene | 15 | 0.11 | 1.36 | 4.60 |
| ethyl benzene | 15 | 0.25 | 1.76 | 5.32 |
| isopropyl chloride | 15 | 1.30 | 1.50 | 5.09 |
| isopropyl alcohol | 15 | 3.66 | 2.34 | 7.78 |
| n-heptane | 29 | 8.25 | 1.08 | 5.18 |

[a] Total ion figures were corrected for excess-kinetic-energy ions before percentages were computed.

Table V. Numerical Values of Parameters Appearing in Equations 2 and 3.

| parameter | $k_1$ | $k_2$ | $w_1$(cm) | $l_1$(cm) | $L_1$(cm) | $L_2$(cm) |
|---|---|---|---|---|---|---|
| value | 3.0 | 2.0 | 0.00762 | 0.3175 | 0.635 | 39.898 |

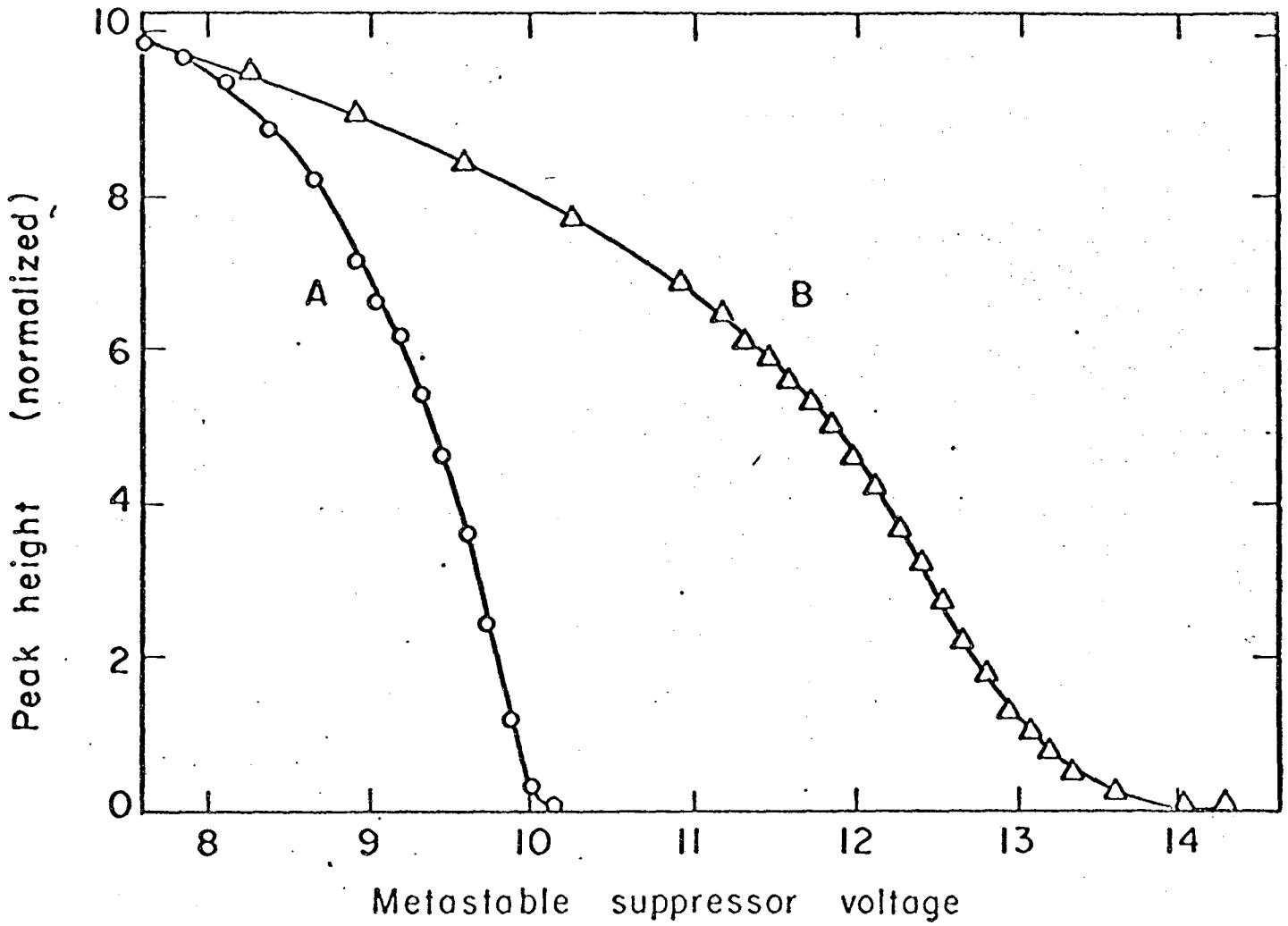
Table VI. Comparison of Calculated with Observed Excess-Kinetic-Energy Methyl Ion Appearance Potentials.

| Compound | A.P. Meas. | Total K.E. (calc.)[a] | A.P. for[b] complementary thermal ion | A.P.[c] Calc. |
|---|---|---|---|---|
| ethane | 30.3 | 4.90 | 13.95 | 28.65 |
| propane | 30.8 | 4.02 | 15.3 | 29.15 |
| n-butane | 29.7 | 3.35 | 13.15 | 26.3 |
| isobutane | 29.4 | 3.59 | 13.6 | 27.0 |
| n-pentane | 28.1 | 2.83 | 14.2 | 26.85 |
| neopentane | 29.5 | 3.42 | 14.9 | 28.1 |

[a] Calculated from measured $CH_3^+$ ion energies assuming C-C bond cleavage occurs first and little or no kinetic energy is involved in $H_2$ elimination.

[b] i.e. for process $C_nH_{2n+2}^{+e^-} \longrightarrow CH_3^+ + H_2 + C_{n-1}H_{2n-3}^+ + 2e^-$ (values from ref. 15)

[c] Assuming overall mechanism is $C_nH_{2n+2}^{++} \longrightarrow CH_3^+ + H_2 + C_{n-1}H_{2n-3}^+ + K.E.$




MU-29872

Figure 1. Variation of peak heights with metastable-suppressor voltage. Data taken at 0-V repellers and 300-V accelerating voltage. A: Curve for thermal M/q = 20 peak from neon; B: Curve for 2.66-eV excess-kinetic-energy M/q = 15 peak from isobutane.

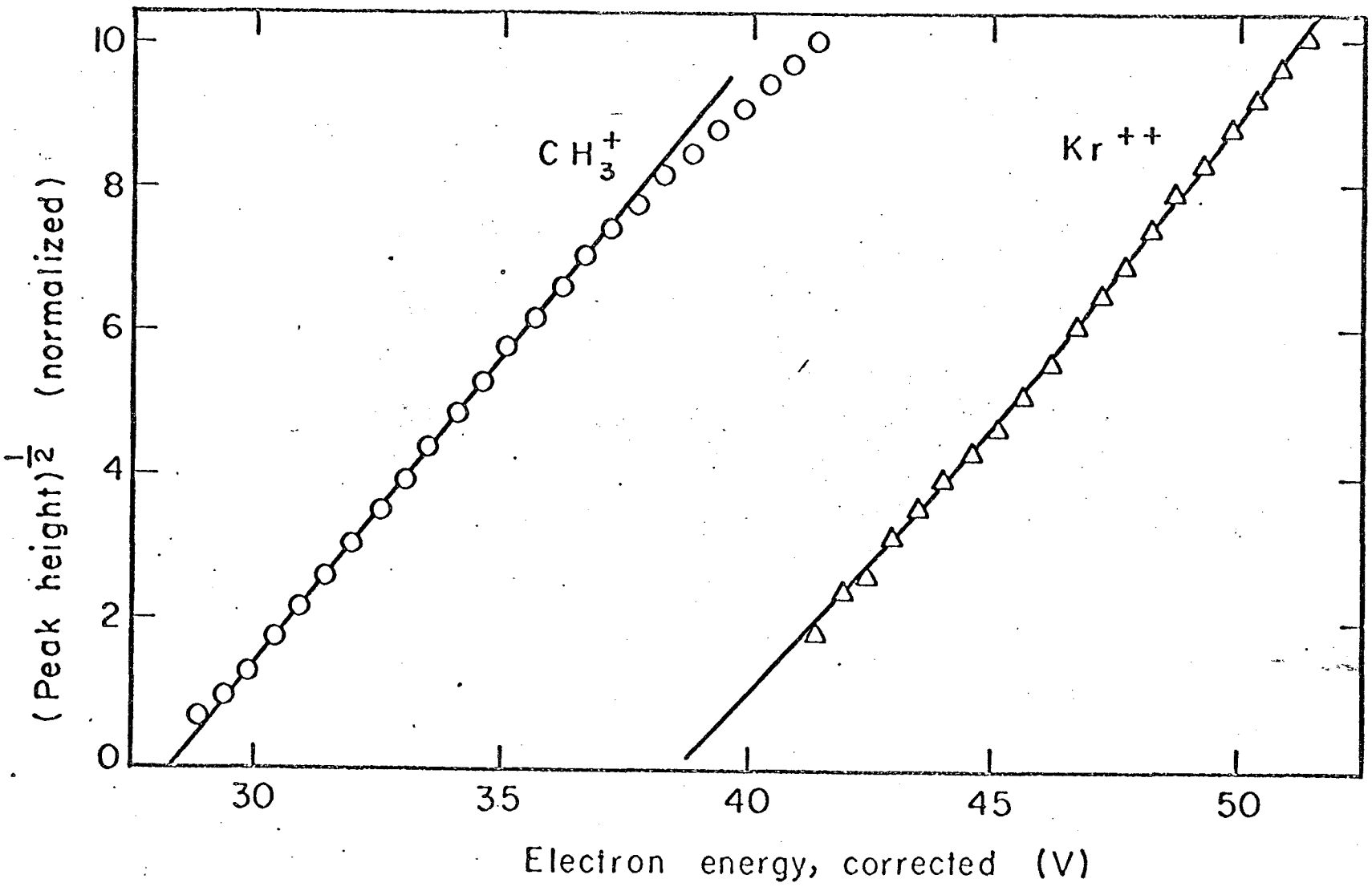



Figure 2. Ionization efficiency curves for $Kr^{++}$ and excess-kinetic-energy $CH_3^+$ ions from a krypton-benzene mixture.

MU-30560

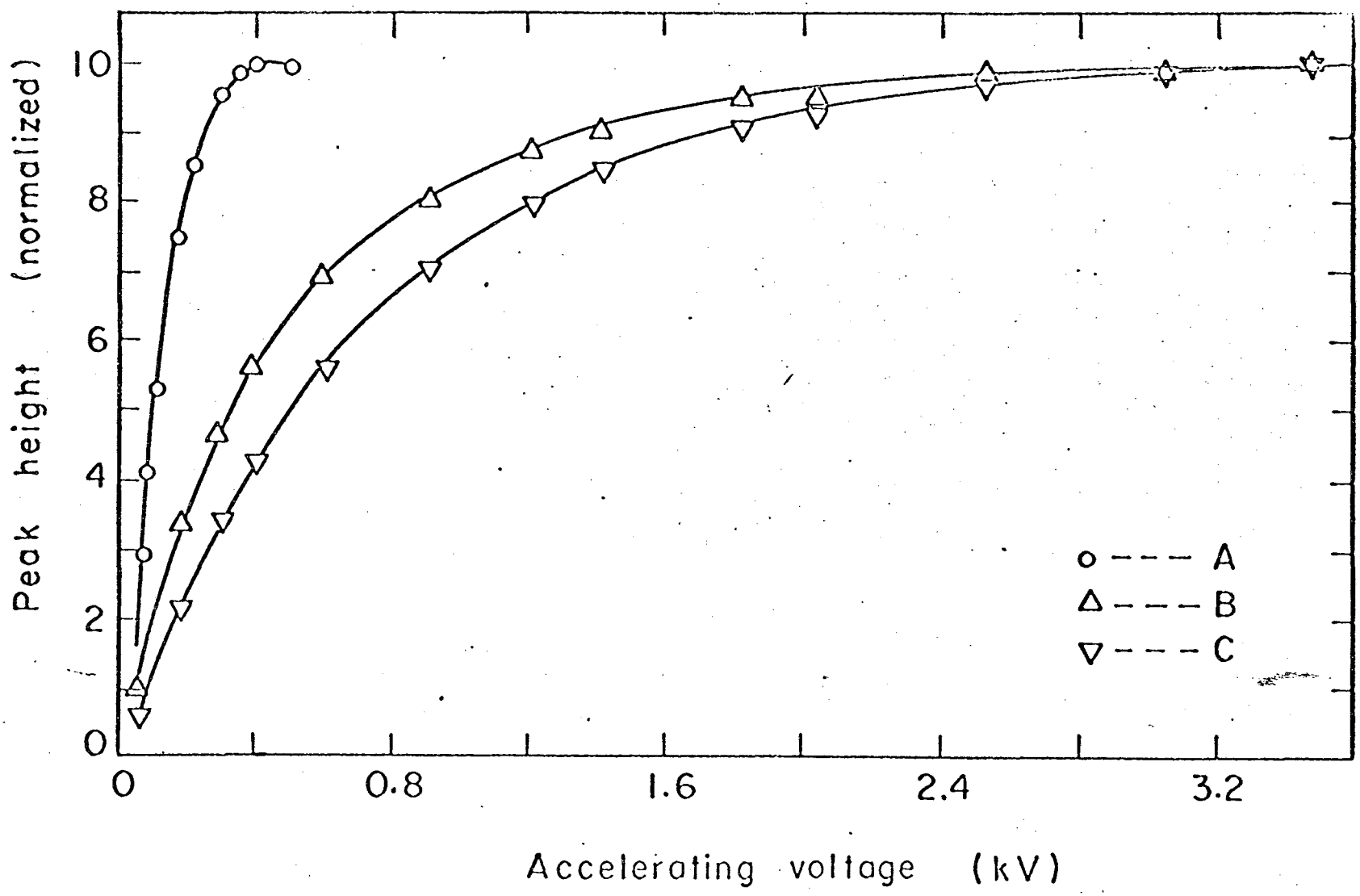



Figure 3. Variation with accelerating voltage of peak heights for near-thermal ions of M/q = 15. Data taken with repeller voltage at 1% of accelerating voltage. A: Curve for thermal ions (methane); B: Curve for 0.15-eV ions (methanol); C: Curve for 0.25-eV ions (methyl chloride).

MU-29875

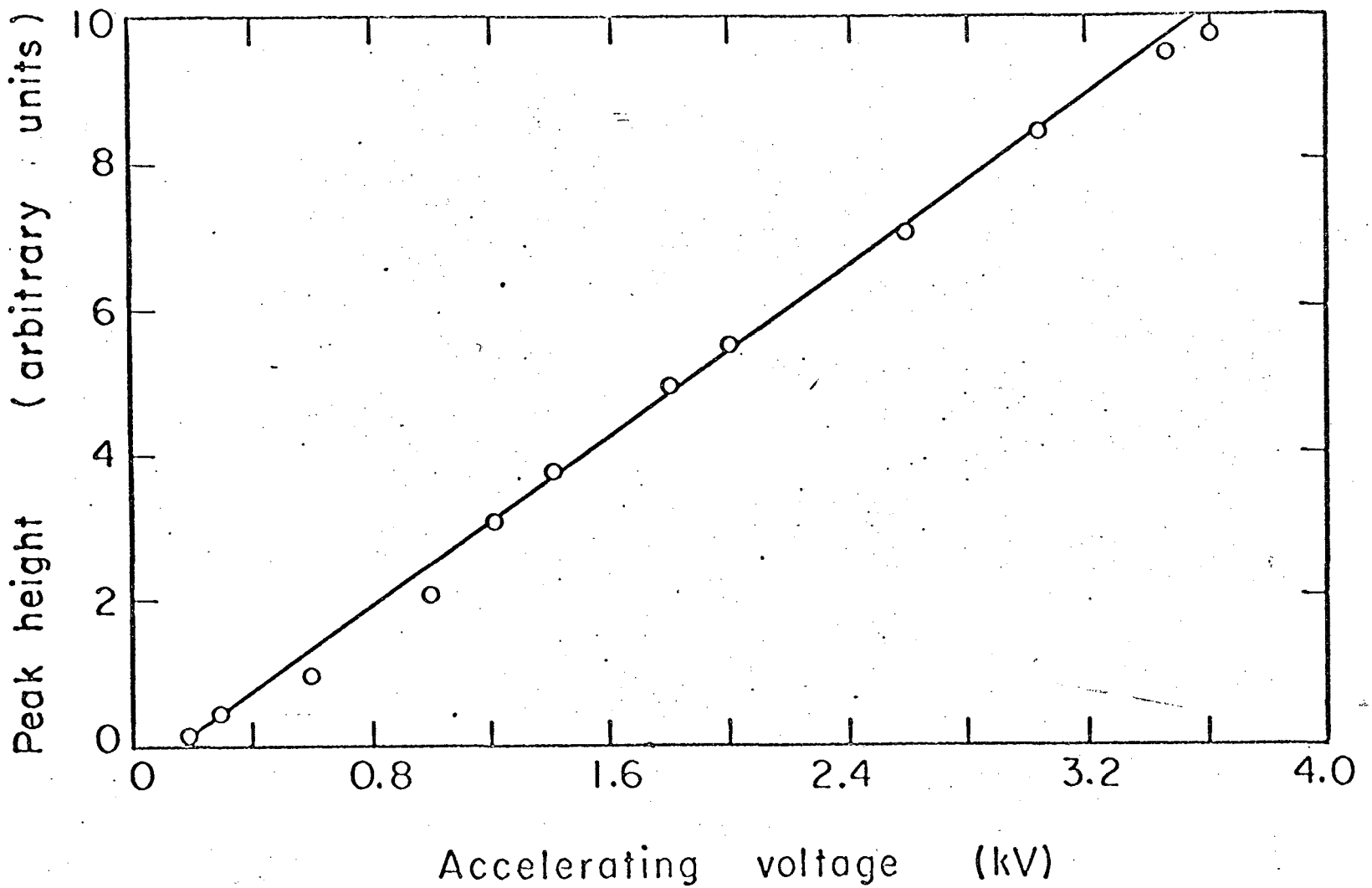



Figure 4. Computed variation with accelerating voltage of peak height of excess-kinetic-energy M/q = 15 ion peak from propane. MU-29876

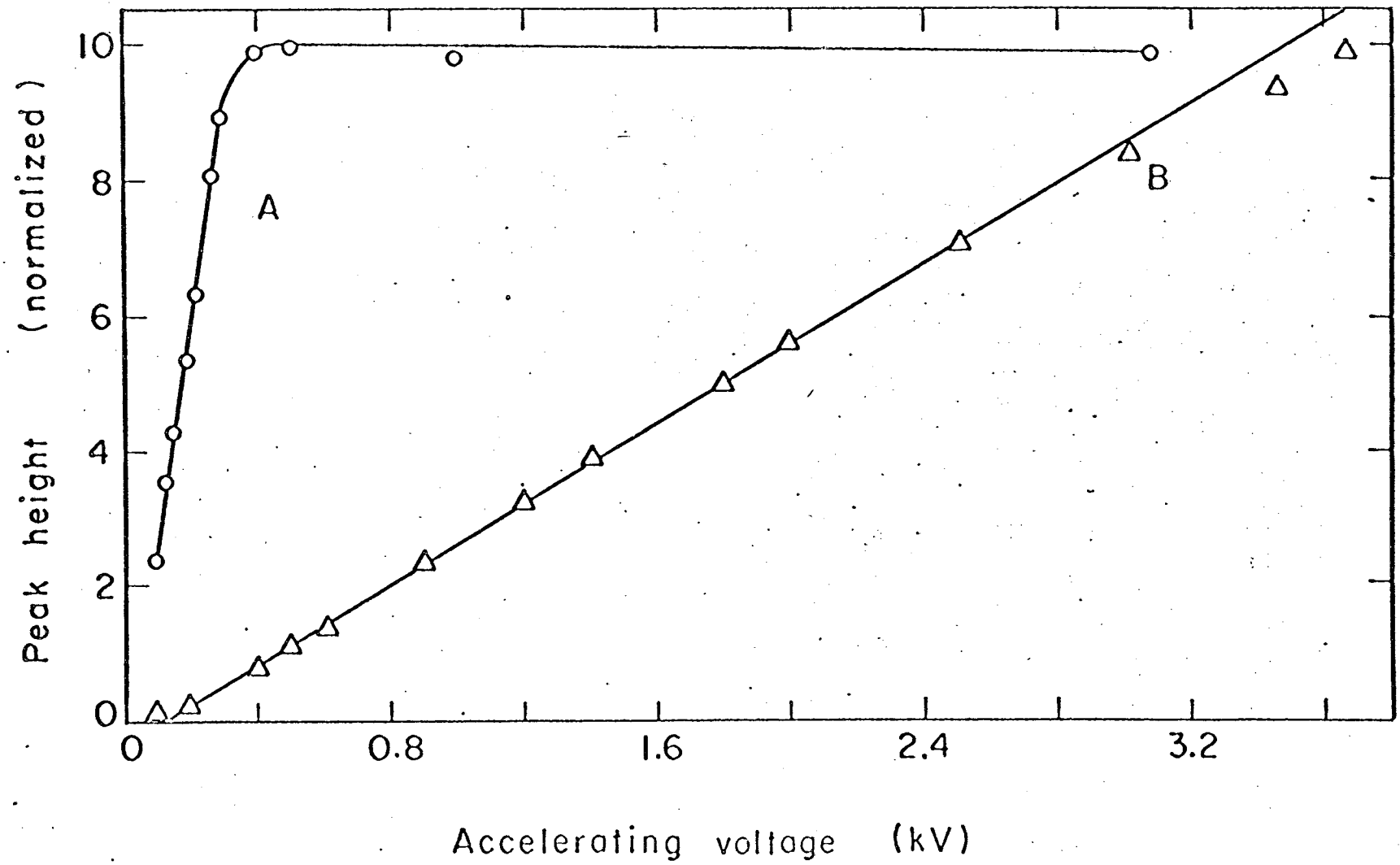



Figure 5. Variation of peak heights with accelerating voltage. Data taken with repeller voltage at 1% of accelerating voltage. A: Curve for thermal M/q = 15 peak from methane; B: Curve for 2.27-eV excess-kinetic-energy M/q = 15 peak from benzene.

MU-29873

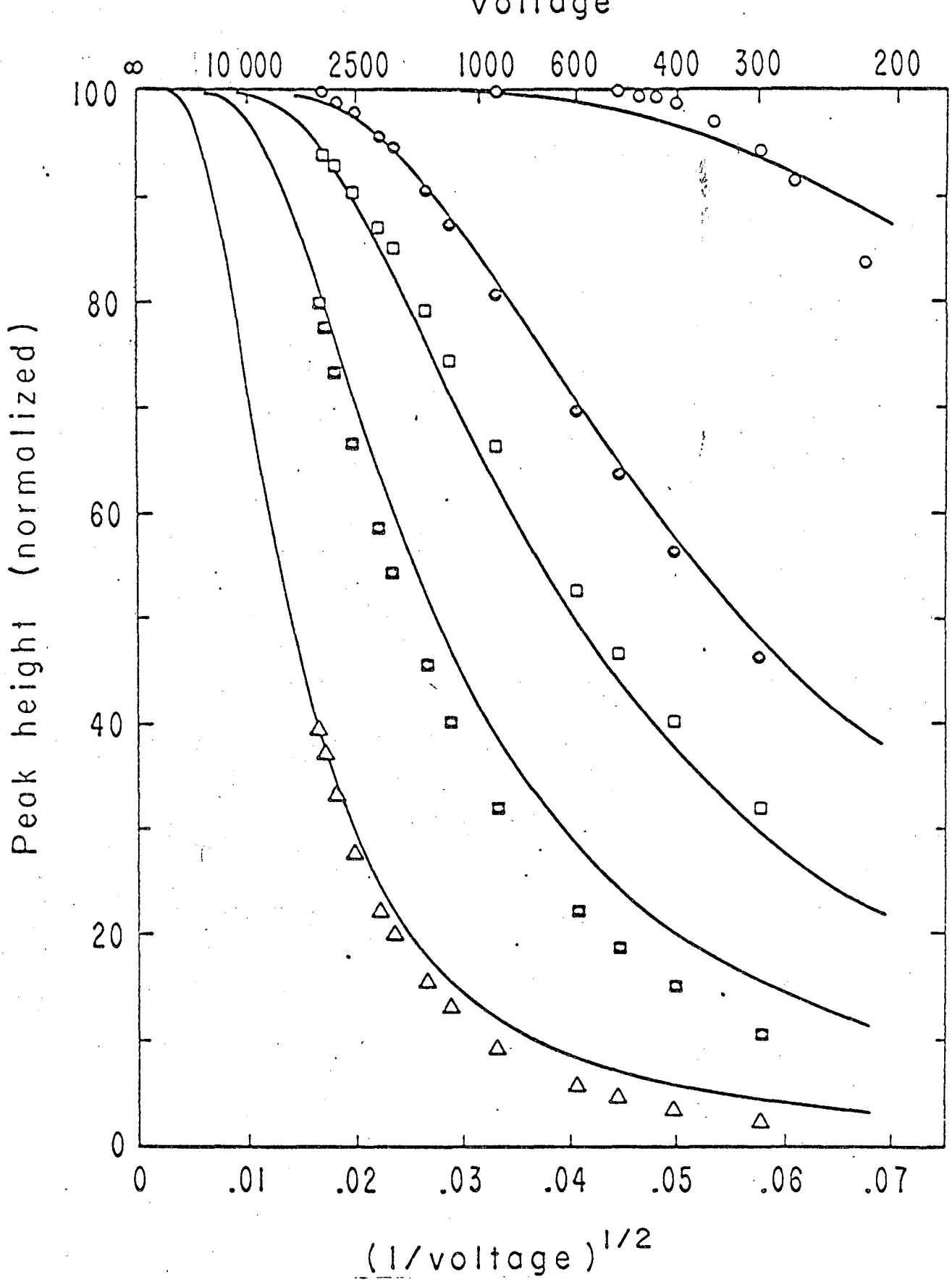



Figure 6. Comparison of theory with experiment: discrimination of the mass spectrometer against methyl ions of different kinetic energies (in eV), as a function of the accelerating voltage. Points are experimental; smooth curves are theoretical. The source compound for the methyl ions and the kinetic energies of the ions, are as follows: ○ - $CH_4$ (thermal); ◐ - $CH_3OH$ (0.14 eV); □ - $CH_3Cl$ (0.27 eV); ■ - $CH_3F$ (0.58 eV); △ - $C_6H_6$ (2.27 eV).

MU-31791

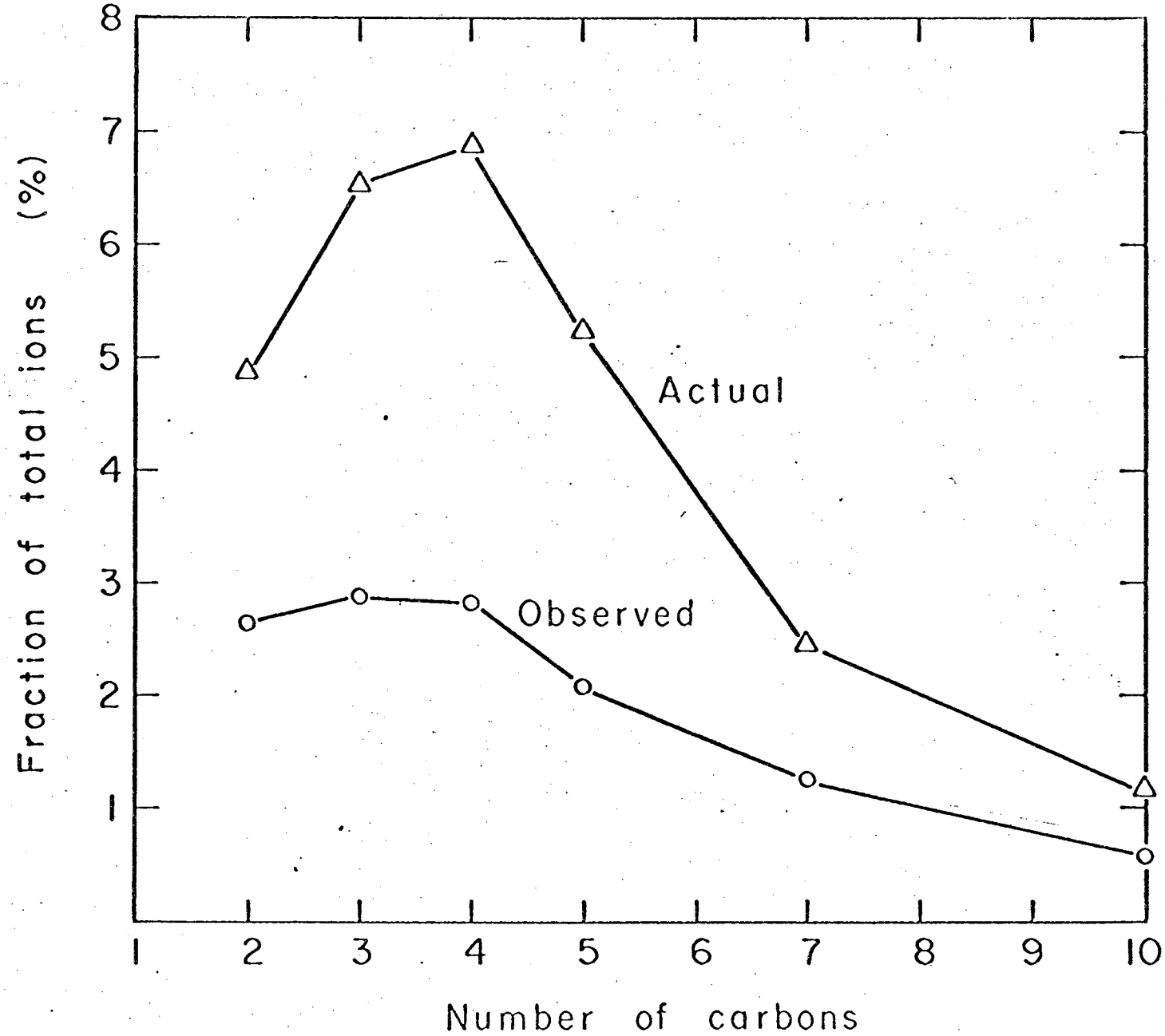



Figure 7. Comparison, for normal aliphatic hydrocarbons, of observed percentage of methyl ions in mass spectra with actual percentage formed by electron impact (for 70-V electrons). MU-31790

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