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The Decomposition of Neopentane under Electron Impact

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Appearance potentials are reported for the formation by electron impact of these various ions from neopentane: t-$C_4H_9^+$, $C_3H_5^+$, $C_3H_3^+$, $C_2H_5^+$, $C_2H_3^+$, CH_3^+. Where possible ionization processes and/or heats of formation are deduced. The heat of formation of t-$C_4H_9^+$ is found to be 179 kcal./mole, which disagrees with the heretofore accepted value. The heat of formation of t-butyl radical is found to be about 2 kcal./mole, which agrees with published values within the limits of our experimental accuracy. The new $\Delta H_f(t\text{-}C_4H_9^+)$ value is used to make a re-interpretation of the previously published value of the appearance potential of t-butyl ion from 3,3-dimethyl-1-butene, and from the re-interpretation one can deduce for the quantities $\Delta H_f(C_2H_3)$ and $D(C_2H_3\text{–}H)$ the values 68 and 107 kcal./mole, respectively. The evidence concerning the neopentane decomposition modes provided by metastable ions is considered, and it is found that the metastable ion evidence and appearance potential evidence for the reactions producing the mass 27 and 39 ions are not in agreement. A discussion of the possible origins of the disagreement is given.

We wish to report here the results we have obtained recently on the energetics of the important modes of decomposition of neopentane under electron impact.

Experimental

Appearance potentials were determined using the conventional vanishing current method[1] in our Westinghouse Type LV mass spectrometer. The electron voltage scale was calibrated by means of krypton. The pertinent operating conditions were: electron current = 3 μamp., ion repeller = 1.9 v., ion accelerating voltage = 600 v., ionization chamber temperature = *ca.* 270°, minimum detectable ion current = 1×10^{-15} amp.

Five or six replicate determinations of the ionization efficiency curves involved in each appearance potential determination were made, and the appearance potentials listed in Table I are derived by averaging the critical potentials obtained from the several replicate runs. Acceptable agreement between replicate measurements was obtained. As a matter of interest, we also include in Table I the relative abundances (percentage of total ionization) of the several ions in the neopentane mass spectrum as calculated from the API Catalog of Mass Spectral Data.

TABLE I

APPEARANCE POTENTIALS OF NEOPENTANE IONS

Mass	Rel. intensity (%)	AP (e.v.)
57	40.6	10.83
41	16.8	13.13
39	5.4	17.08
29	15.6	13.81
27	6.4	17.95
15	2.6	13.14, 20.67

Results and Discussion

The results for the several ions will be discussed individually in the following paragraphs.

M = 57, t-$C_4H_9^+$, A = 10.83 v. = 250 Kcal./mole.—The ionization reaction producing t-$C_4H_9^+$ from neopentane is undoubtedly neo-C_5H_{12} = t-$C_4H_9^+$ + CH_3 (omitting the electrons involved for ease of writing). Using this reaction the observed appearance potential corresponds to a value of 179 kcal./mole for the heat of formation of t-butyl ion. Our appearance potential is higher than the value of $A(t\text{-}C_4H_9^+)$ = 10.29 v. reported several years ago by Stevenson.[2] The t-butyl ion heat of formation corresponding to this latter appearance potential is 165 kcal./mole. However, very recently Lossing and co-workers have made a direct measurement of the ionization potential of t-butyl radical, and they obtained[3] the value $I(t\text{-}C_4H_9)$ = 7.42 v. = 171 kcal./mole. Values for $\Delta H_f(t\text{-}C_4H_9)$ in the range 3–6 kcal./mole have been reported,[1] which when combined with Lossing's t-butyl ionization potential give $\Delta H_f(t\text{-}C_4H_9^+)$ values in the range 174–177 kcal./mole. The agreement with the value derived from our neopentane appearance potential is satisfactory and leads us to think that Stevenson's value is somewhat low.

This new value of $\Delta H_f(t\text{-}C_4H_9^+)$ enables us to modify a distressingly high value of $D(C_2H_3\text{–}H)$ which was reported some years ago.[4] This value is obtained from the measured appearance potential (11.30 v.) of the t-butyl ion produced from 3,3-dimethyl-1-butene according to the reaction C_6H_{12} = t-$C_4H_9^+$ + C_2H_3. The observed appearance potential when combined with the new value of $\Delta H_f(t\text{-}C_4H_9^+)$ gives for $\Delta H_f(C_2H_3)$ and $D(C_2H_3\text{–}H)$ the values 68 and 107 kcal./mole, respectively, which we at one time would have thought to be more reasonable than the original values of 81 and 119 kcal./mole which result from the use of 165 kcal./mole for $\Delta H_f(t\text{-}C_4H_9^+)$. However, very recently Reed and Thornley[5] adduce evidence in favor of the old values from measurements of appearance potentials of ions from formaldehyde, acrolein and acetaldehyde. Thus it is unfortunately true that the electron impact value for the heat of formation of vinyl radical is still uncertain.

M = 41, $C_3H_5^+$, A = 13.13 v. = 303 Kcal./mole.—A tabulation of the allyl ion heats of formation shows that the values fall into two distinct groups: namely, those around 220 kcal./mole and those in the range 230–235 kcal./mole. The ions in the first group are formed by direct ionization of allyl radical or by the decomposition of allyl halides; whereas the ions in the higher energy group are formed from all the other compounds studied. We shall assume that the heat of formation value applicable to the $C_3H_5^+$ ion formed from neopentane is 230 kcal./mole, and in this case the reactions producing the ion with calculated heats of reaction closest to the observed appearance potential are

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(1) See Field and Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

(2) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

(3) F. P. Lossing and J. B. de Sousa, THIS JOURNAL, **81**, 281 (1959).

(4) F. H. Field, *J. Chem. Phys.*, **21**, 1506 (1953).

(5) R. I. Reed and M. B. Thornley, *Trans. Faraday Soc.*, **54**, 949 (1958).

$$\text{neo-}C_5H_{12} \longrightarrow C_3H_5^+ + C_2H_5 + H_2.\ \Delta H = 295 \text{ kcal./mole} \qquad (1)$$

$$\longrightarrow C_3H_5^+ + CH_3 + CH_4.\ \Delta H = 283 \text{ kcal./mole} \qquad (2)$$

$$\longrightarrow C_3H_5^+ + C_2H_6 + H,\ \Delta H = 302 \text{ kcal./mole} \qquad (3)$$

The energy correspondence for reactions 1 and 3 is good, and taking into account just energy considerations we would conclude that the allyl ion is formed from neopentane by either or both of these reactions. However, reaction 2 is not excluded by the energetics. Furthermore, from the fact that neopentane under electron impact produces only a negligible amount of molecule–ion but a copious amount of $C_4H_9^+$, it is clear that the molecule-ion very rapidly decomposes into t-$C_4H_9^+$ + CH_3. One is very tempted to think that t-$C_4H_9^+$ ion is an intermediate in the formation of all ions lighter than mass 57, in which case the allyl ion would be formed by reaction 2. As will be discussed later, such a postulate is supported by metastable ion evidence. If indeed allyl ion is formed by this reaction, the observed appearance potential shows that excess energy is required. We are inclined to choose reaction 2, but the evidence is not unequivocal.

M = 39, $C_3H_3^+$, A = 17.08 v. = 394 Kcal./mole.—The heat of formation of $C_3H_3^+$ ion is given by Collin and Lossing[6] to be 264 kcal./mole, and the ionization reactions producing the $C_3H_3^+$ ion from neopentane with calculated heats of reaction closest to that observed experimentally are

$$\text{neo-}C_5H_{12} \longrightarrow C_3H_3^+ + CH_2 + CH_3 + 2H_2,\quad \Delta H = 395 \text{ kcal./mole} \qquad (4)$$

$$\longrightarrow C_3H_3^+ + CH_2 + CH_4 + H_2 + H,\quad \Delta H = 398 \text{ kcal./mole} \qquad (5)$$

$$\longrightarrow C_3H_3^+ + C_2H_4 + 2H_2 + H,\quad \Delta H = 370 \text{ kcal./mole} \qquad (6)$$

The agreements between the observed and calculated heats of reaction are excellent for both reaction 4 and reaction 5, and in addition reaction 4 can occur by way of the formation of t-$C_4H_9^+$ as an intermediate. On the other hand, these reactions involve the formation of CH_2 radical, which, to the extent of our knowledge, is seldom formed in decomposition processes under electron impact. This, however, is not sufficient reason to reject reaction 4, which is our choice for the reaction involved in the production of $C_3H_3^+$ from neopentane.

M = 29, $C_2H_5^+$, A = 13.81 v. = 318 Kcal./mole.—The heat of formation of ethyl ion is well established at 224 kcal./mole. The only neopentane decomposition reactions yielding calculated heats of reaction close to that observed experimentally are

$$\text{neo-}C_5H_{12} \longrightarrow C_2H_5^+ + C_3H_6 + H,\quad \Delta H = 321 \text{ kcal./mole} \qquad (7)$$

$$\longrightarrow C_2H_5^+ + C_2H_4 + CH_3,\quad \Delta H = 308 \text{ kcal./mole} \qquad (8)$$

The heat of reaction of (7) must be considered as equal to the observed value taking into account experimental error. However, the energy discrepancy for reaction 8 is small enough not to exclude it from consideration. Furthermore, this reaction can proceed through the t-$C_4H_9^+$ ion as an intermediate, and reaction 8 constitutes our choice for the reaction producing ethyl ion.

M = 27, $C_2H_3^+$, A = 17.95 v. = 414 Kcal./mole.—Possible decomposition reactions of neopentane producing vinyl ion at appearance potentials close to that actually observed are

$$\text{neo-}C_5H_{12} \longrightarrow C_2H_3^+ + 3CH_3,\quad \Delta H = 413 \text{ kcal./mole} \qquad (9)$$

$$\longrightarrow C_2H_3^+ + C_2H_6 + CH_2 + H.\quad \Delta H = 411 \text{ kcal./mole} \qquad (10)$$

No choice between these reactions can be made on the basis of energetics, but because of the possibility of the t-$C_4H_9^+$ intermediate, we are inclined to favor reaction 9.

M = 15, CH_3^+, A = 13.14, 20.07 v. = 303, 463 Kcal./mole.—Two appearance potentials for the formation of methyl ion are observed. The process corresponding to the lower potential occurs with a small probability as shown by the fact that the ionization efficiency curve between the lower and upper potentials rises quite slowly. The only neopentane decomposition reaction giving methyl ion at appearance potential of about 303 kcal./mole is

$$\text{neo-}C_5H_{12} \longrightarrow CH_3^+ + t\text{-}C_4H_9,\quad \Delta H = 307 \text{ kcal./mole} \qquad (11)$$

where the heat of reaction is calculated taking $\Delta H_f(t\text{-}C_4H_9)$ = 6 kcal./mole.[1] Thus neopentane exhibits the rather rare behavior of decomposing by a pair of complementary reactions, *i.e.*, by (11) and

$$\text{neo-}C_5H_{12} \longrightarrow t\text{-}C_4H_9^+ + CH_3 \qquad (12)$$

From a comparison of the appearance potentials for reactions 11 and 12, it may be seen that 12 is a low energy and 11 a high energy process. It is of interest, then, that in accord with what one would predict from the Eyring quasi-equilibrium theory of mass spectra (see ref. 1), reactions 11 and 12 occur with low and high probabilities, respectively.

If one grants that methyl ion is produced at the lower appearance potential by reaction 11, it is of interest to turn the energetic calculation around and calculate the heat of formation of t-butyl radical from the observed appearance potential. A value of about 2 kcal./mole is thus obtained for $\Delta H_f(t\text{-}C_4H_9)$, which is one of the same order of magnitude as the previously reported values.[1] It must be recognized that because of the low intensity of the methyl ion associated with the first appearance potential, we cannot claim a high degree of accuracy for this heat of formation value.

It is not possible to identify the reaction producing the methyl ions formed at the higher appearance potential. One can write about twenty fairly reasonable reactions producing methyl ion from neopentane and, of these, seven occur at calculated appearance potentials close to that observed experimentally. No choice of reaction can be made.

It is of interest to consider the information concerning the decomposition modes of neopentane which can be deduced from the metastable ions

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[6] J. Collin and F. P. Lossing, THIS JOURNAL, 80, 1570 (1958); see also, *ibid.*, 79, 5848 (1957).

observed in the mass spectrum of neopentane.[7] From the apparent mass number of the metastable peak, the mass of the product ion and the reactant ion can be calculated, and from this information it is oftentimes a simple matter to deduce the nature of the decomposition reaction occurring.

According to the neopentane mass spectrum published in API Catalog of Mass Spectral Data (serial No. 8),[8] metastable ions are to be observed at apparent masses 37.1, 29.5 and 25.1, which correspond to the metastable ion transitions $41^+ = 39^+ + 2$, $57^+ = 41^+ + 16$, and $29^+ = 27^+ + 2$. We have also observed these metastable ions in our laboratory using our Westinghouse mass spectrometer. Following presently accepted theories of the ionization and dissociation under electron impact, we postulate that these transitions imply that the following reactions are among those involved in the decomposition of neopentane.

$$C_3H_5^+ \longrightarrow C_3H_3^+ + H_2 \qquad (13)$$

$$C_4H_9^+ \longrightarrow C_3H_5^+ + CH_4 \qquad (14)$$

$$C_2H_5^+ \longrightarrow C_2H_3^+ + H_2 \qquad (15)$$

It is, in our opinion, of very great interest that disagreement exists between the conclusions to be drawn from the metastable ion evidence concerning decomposition reactions and the appearance potential evidence. From reaction 14 one infers that the allyl ion is formed from neopentane by the reaction sequence

$$\begin{aligned}\text{neo-}C_5H_{12} &\longrightarrow C_4H_9^+ + CH_3\\ &\quad\llcorner\!\longrightarrow C_3H_5^+ + CH_4 \qquad (16)\end{aligned}$$

which over-all is identical with reaction 2 and quite compatible with the observed appearance potential for the mass 41 ion. Thus, in this case agreement is found. However, reaction 13 implies that the $C_3H_3^+$ ion is formed by the reaction sequence

$$\begin{aligned}\text{neo-}C_5H_{12} &\longrightarrow C_4H_9^+ + CH_3\\ &\quad\llcorner\!\longrightarrow C_3H_5^+ + CH_4 \qquad (17)\\ &\qquad\quad\llcorner\!\longrightarrow C_3H_3^+ + H_2\end{aligned}$$

but this does not correspond to any one of the reactions 4, 5 or 6, which from the appearance potential measurements are considered most probably to be involved in the formation of the $C_3H_3^+$ ion. Similarly, reaction 15 implies that the $C_2H_3^+$ ion is formed from neopentane by the reaction sequence

$$\begin{aligned}\text{neo-}C_5H_{12} &\longrightarrow C_4H_9^+ + CH_3\\ &\quad\llcorner\!\longrightarrow C_2H_5^+ + C_2H_4 \qquad (18)\\ &\qquad\quad\llcorner\!\longrightarrow C_2H_3^+ + H_2\end{aligned}$$

but this does not correspond to either of the reaction possibilities (reactions 9 and 10) deduced from the appearance potential measurements.

The metastable ions are observed at an ionizing voltage of about 75 volts, and the discrepancy in the reactions producing masses 29 and 39 might be the result of the possibility of the metastable ion processes being of higher energy than the minimum energy processes determined by the appearance potential measurements. However, from tabulated energies[1] one calculates that the minimum heat of reaction for reaction 17 is 318 kcal./mole and that for reaction 18 is 364 kcal./mole. By contrast the appearance potentials for the mass 39 and 27 ions are 394 and 414 kcal./mole, respectively. Thus this explanation for the discrepancies is untenable.

A second possible explanation for the discrepancies is that activation barriers in excess of minimum endothermicities exist, and thus the appearance potentials measured refer to the formation of excited decomposition products. However, in the case of vinyl ion assumed to be produced by reaction 18, it is evident that the reaction sequence involves the formation of $C_2H_5^+$ by the reaction deduced from the ethyl ion appearance potential (reaction 8). By comparison of the observed appearance potential and the calculated endothermicity of reaction 8, it may be concluded that the ethyl ion is formed with an excitation energy of 10 kcal./mole. The vinyl ion is formed according to reaction 18 by the elimination of H_2 from ethyl ion, a process which conceivably might involve an activation energy. However, an inspection of the vinyl ion heats of formation tabulated in ref. 1, pp. 252–253, shows rather conclusively that this decomposition of ethyl ion to form vinyl ion occurs with at the most a few kcal./mole activation energy. Thus the total excess energy to be anticipated in reaction 18 on the basis of rather firm considerations is 10–20 kcal./mole which is to be compared with the difference of 50 kcal./mole between the calculated minimum endothermicity of reaction 18 and the observed mass 27 appearance potential. Similar considerations apply to the mass 39 ion. Thus the activation energy explanation for the discrepancies is untenable.

A third possible explanation lies in the relative amounts of energy needed according to the quasi-equilibrium theory of mass spectra (see ref. 1, pp. 68–79) to product normal fragment ions and metastable ions. Metastable ions are considered to be formed from precursor ions with a smaller amount of excitation energy than that in the precursors of normal fragment ions. As a result the decomposition rate in the first case is smaller and produces fragment ions in the metastable region of the mass spectrometer. From the dimensions of our mass spectrometer and the voltages involved in its operation, we calculate that the minimum unimolecular decomposition rate constant for the production of normal fragment ions is 2.3×10^6 sec.$^{-1}$. With this rate constant 99% of the ions initially formed in the electron bombardment will decompose before leaving the ionization chamber. Similarly, the maximum number of metastable ions is formed when the decomposition rate constant of the precursor ion has the value 3.5×10^5 sec.$^{-1}$, and with this value of the rate constant about 25% of the ions formed in the electron beam will appear as metastable ions.

Let us now apply these considerations to the postulated formation of $C_2H_3^+$ from $C_2H_5^+$. We will make the assumption that the processes yielding ethyl ion occur rapidly enough so that the

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(7) The consideration of metastable ion evidence was suggested by the referee of the original version of this paper for which we thank him. For general background information on metastable ions, see ref. 1, pp. 194–202.

(8) American Petroleum Institute Research Project 44, Catalog of Mass Spectral Data, Carnegie Institute of Technology, Pittsburgh, 1953.

normal and metastable fragment ion rate constants calculated in the preceding paragraph can be used. We think that the results thus obtained will not be badly in error. From the quasi-equilibrium theory we write

$$k = A\left(\frac{E - e_0}{E}\right)^{N - L/2 - 1}(E - e_0)^{(L - L^{\ddagger})/2} \quad (19)$$

where E is the excitation energy of the reactant ion, e_0 is the activation energy for the process in question, N is the number of oscillators and L the number of free rotors in the product ion, $L^{\ddagger}$ is the number of free rotors in the activated complex, and A is a constant involving vibrational frequencies, moments of inertia, numbers of oscillators and rotors and miscellaneous constants. For the reaction $C_2H_5^+ = C_2H_3^+ + H_2$, $N = 15$, $L = 1$, $L^{\ddagger} = 0$, $e_0 = 55$ kcal./mole, and, according to Rosenstock, Wahrhaftig and Eyring[9] $A = 2.653 \times 10^{19}$. Then

$$k = 2.653 \times 10^{19}\left(\frac{E - e_0}{E}\right)^{13.5}(E - e_0)^{1/2} \quad (20)$$

Values of $(E - e_0)/E^{13.5}(E - e_0)^{1/2}$ were calculated as a function of E and plotted. From the plot and equation 20 the values of E corresponding to the rate constant for metastable fragment ion formation and that for normal fragment ion formation were calculated. The values obtained were, respectively, $E_{\text{meta}} = 60.3$ kcal./mole and $E_{\text{normal}} = 61.2$ kcal./mole. This 0.9 kcal./mole is the difference in energy content of the ethyl ions producing metastable and normal vinyl ions. However, a more meaningful quantity for our purposes is the difference in energy which must be provided a neopentane molecule to produce an energy difference of 0.9 kcal./mole in ethyl ion. Assuming that in a decomposition process excess energy divides between fragments in proportion to the number of vibrational degrees of freedom, it can be calculated on the basis of reaction 18 that 47% of any excess energy in a neopentane molecule will appear in the ethyl ion. Thus the 0.9 kcal./mole difference in energy in ethyl ion corresponds to about 2 kcal./mole difference in the amount of energy given a neopentane molecule. This is trivially small and cannot account for the observed difference of 50 kcal./mole between the minimum endothermicity of the postulated process that includes the metastable transition and the observed appearance potential of the vinyl ion.

Similar calculations were made for the reaction $C_3H_5^+ = C_3H_3^+ + H_2$ and, as a matter of interest, for t-$C_4H_9^+ = C_3H_5^+ + CH_4$. In the first reaction it was assumed that the product ion has the propargyl structure, that the vibrational frequencies of importance are the same as those given by Rosenstock, Wahrhaftig and Eyring[8] for $C_2H_4^+ = C_2H_2^+ + H_2$ and that no free rotation of the CH_2 groups in allyl ion occurs. The activation energy is 45 kcal./mole. The energies corresponding to the metastable and normal fragment ions are 67.8 and 72.0 kcal./mole, respectively. Taking into account energy division in preceding processes, this difference of 4.2 kcal./mole in the energy of allyl ion would require 7.5 kcal./mole in the neopentane molecule. In the case of the t-butyl ion decomposition the Rosenstock, Wahrhaftig and Eyring treatment of the reaction $C_3H_8^+ = C_2H_4^+ + CH_4$ was followed as much as possible. The reactant ion has 33 vibrational modes and three internal rotations. One rotation is considered to become a torsional vibration in the activated complex. The activation energy is 41 kcal./mole. The energies corresponding to the metastable and normal fragment ions are 58.9 and 60.5 kcal./mole, respectively. Taking into account energy division in preceding processes, this difference of 1.6 kcal./mole in the energy of t-butyl ion would require 1.9 kcal./mole in the neopentane molecule.

In the case of the $C_3H_3^+$ ion the difference between the minimum endothermicity of the postulated process including the metastable transition (reaction 17) and the observed appearance potential of the $C_3H_3^+$ ion is 76 kcal./mole, and only 7.5 kcal./mole of this can be accounted for on the basis of the different excitation energy hypothesis.

It is possible to reconcile the metastable ion and appearance potential evidence by postulating that the metastable reactions producing the $C_2H_3^+$ and $C_3H_3^+$ ions are not reactions 13 and 15, respectively; but rather are

$$C_3H_5^+ \longrightarrow C_3H_3^+ + 2H \quad (21)$$

and

$$C_2H_5^+ \longrightarrow C_2H_3^+ + 2H$$

The minimum energies to produce $C_3H_3^+$ and $C_2H_3^+$ from neopentane by means of sequences including reactions 21 and 22 are 422 and 468 kcal./mole, respectively. These energies are larger than the observed appearance potentials (394 and 414 kcal./mole, respectively), and thus the sequences including reactions 21 and 22 would not occur at the appearance potentials. The proof of this postulate concerning the metastable reactions requires a determination of the appearance potentials of the metastable ions in question, but unfortunately we are for the present unable to make these measurements.

Even if reactions 21 and 22 are in fact involved in the formation of the metastable ions, there remains unanswered the interesting question of why the much less energetic reactions 17 and 18 do not occur. We can illuminate this question only to the extent of pointing out that this lack of occurrence can hardly be reconciled with a theory in which a continuum or near continuum of energy states is postulated for the reactant ion and all the intermediate ions which may be involved in the formation of a given product ion.

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[9] H. M. Rosenstock, A. L. Wahrhaftig and H. Eyring, "The Mass Spectra of Large Molecules, II. The Application of Absolute Rate Theory," Tech. Report No. II, June 25, 1952, University of Utah, Inst. for Study of Rate Processes, Salt Lake City, pp. 71–72.