

The Dissociation of Ethane by Electron Impact

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The dissociation of C_2H_6 by electron impact has been investigated with a new mass spectrometer. One negative, two doubly-charged and fourteen positive ions have been observed corresponding to the various states of dissociation of the C_2H_6 molecule. An analysis is given of the processes taking place in the upper mass-range where unique interpretations of the results may be made. The difficulty of accurately determining the relative intensities of two ions having a large difference in mass is discussed as well as the meaning of the probable errors given for the measured appearance potentials.

IN several recent papers¹⁻³ it has been shown that interesting interpretations may be made of the electron dissociation processes in the more complicated molecules. These papers provide an introduction to this field as well as a review of the previous literature on the subject. The present paper represents an extension of this work to ethane.

The analysis of ethane was made with the new mass spectrometer described in the previous paper. The ions observed are listed in Table I. Mass spectra with this gas in the apparatus were given in the preceding paper along with the description of the apparatus. The fact that the ratio of the intensities of masses 30 and 15 is 100/9 serves to correlate the two mass ranges shown. The height of the mass 28 peak relative to mass 30 is interesting inasmuch as it shows that, for this molecule, it is more probable to strip off an electron and two hydrogen atoms than a single electron. A similar effect was found by Stewart and Olson⁴ in propane and butane. A measurement of the appearance potential indicates that mass 16 is partly due to a methane impurity in the ethane. Of course the peaks at masses 18 and 17 come from water vapor.

In the discussion of the results the same notation will be used as in the previous papers on this subject which were mentioned above:

$A(X^+) \equiv$ Appearance potential of the ion X^+

$I(X) \equiv$ Ionization potential of X

¹ Smith, *Phys. Rev.* **51**, 263 (1937).

² Bleakney, Condon and Smith, *J. Phys. Chem.* **41**, 197 (1937).

³ Kusch, Hustrulid and Tate, *Phys. Rev.* **52**, 843 (1937).

This paper will henceforth be referred to as K, H and T.

⁴ Stewart and Olson, *J. Am. Chem. Soc.* **53**, 1236 (1931).

$D(X) \equiv$ Energy of dissociation of X to atoms in the gaseous state.

$W(X^+) \equiv$ Excess energy (kinetic or excitational) appearing in the production of the ion X^+ from the parent molecule.

The first step in the analysis of the data is the calculation of the energies of the possible states of combination in which two carbon and six hydrogen atoms may exist. In methane there were nine states with which to deal and in ethylene twenty-three. In ethane there are forty-three possible combinations; and as a result, it was only possible to make a significant analysis of the data for the heavier masses. Only the combinations which are in the range in which interpretations were made are given in Table II. Most of the energies listed are obtained from Table VII of Kusch, Hustrulid and Tate using the value 25.0 volts for the state $2C+6H$ referred to C_2H_6 as zero.⁵ The only state that cannot be obtained in this way is C_2H_5+H ; this energy is taken as 2.9 volts, interpolated in the same manner as was done in ethylene.

$C_2H_6^+$. The ionization potential of C_2H_6 is 11.6 ± 0.1 volts. Morris⁶ measured the ionization potentials of C_2H_2 , C_2H_4 and C_2H_6 as 12.3, 12.2 and 12.8 volts, respectively. Since the values for C_2H_2 and C_2H_4 were later determined spectroscopically to be 11.35 and 10.41 volts, Mulliken⁷ suggested as a probable corrected experimental value 11.4 volts for C_2H_6 and felt that this was in reasonable agreement with the spectroscopic estimate. In a very early paper, Hughes and

⁵ Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1936).

⁶ Morris, *Phys. Rev.* **32**, 942 (1928).

⁷ Mulliken, *J. Chem. Phys.* **3**, 517 (1935).

TABLE II. Energies of possible states of combination in which two carbon and six hydrogen atoms may exist.

STATE	ENERGY (VOLTS)
2C+6H	25.0
CH ₃ +C+3H	14.4
CH ₃ +C+H ₂ +H	9.9
CH ₃ +CH+2H	10.9
CH ₃ +CH+H ₂	6.4
CH ₃ +CH ₂ +H	7.4
CH ₃ +CH ₃	3.8
C ₂ +6H	19.5
C ₂ +H ₂ +4H	15.0
C ₂ +2H ₂ +2H	10.6
C ₂ +3H ₂	6.1
C ₂ H+5H	15.7
C ₂ H+H ₂ +3H	11.2
C ₂ H+2H ₂ +H	6.8
C ₂ H ₂ +4H	12.2
C ₂ H ₂ +H ₂ +2H	7.1
C ₂ H ₂ +2H ₂	3.3
C ₂ H ₃ +3H	8.9
C ₂ H ₃ +H ₂ +H	4.4
C ₂ H ₄ +2H	5.8
C ₂ H ₄ +H ₂	1.3
C ₂ H ₅ +H	2.9
C ₂ H ₆	0.0

Dixon⁸ measured the appearance potential of C₂H₆ as 10 volts.

C₂H₅⁺. Since this ion appears at $A(C_2H_5^+) = 12.7$ volts, the energy relation may be written

$$I(C_2H_5) + W(C_2H_5^+) + 2.9 = 12.7 \text{ volts.}$$

This leads to an upper limit for the ionization potential

$$I(C_2H_5) \leq 9.8 \text{ volts.}$$

⁸ Hughes and Dixon, Phys. Rev. **10**, 495 (1917).

C₂H₄⁺. Using the value of $I(C_2H_4) = 10.8$ volts obtained by K, H and T, it is evident that the process here must be

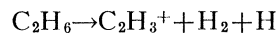


since the calculated energy required in this case is $10.8 + 1.3 = 12.1$ volts in agreement with the appearance potential observed. This means that $W(C_2H_4^+) = 0$ within the limits of error. The process



requiring a minimum of 16.6 volts may possibly occur, but the ionization curve is rising too rapidly in this region as a function of the electron velocity to detect a second break.

C₂H₃⁺. Of the two processes possible here, the one of lower energy appears to be the one that occurs. This is



K, H and T showed that

$$I(C_2H_3) \leq 11.0 \text{ volts.}$$

If it is assumed that $I(C_2H_3) = 11.0$ volts, then the minimum energy calculated for the above process is $11.0 + 4.4 = 15.4$ volts agreeing very well with the observed appearance potential $A(C_2H_3^+) = 15.2 \pm 0.3$ volts. This means that either the ion C₂H₃⁺ is formed from both C₂H₆ and C₂H₄ with the same additional energy

TABLE I. Ions observed in ethane.

ION	ABUNDANCE	APPEARANCE POTENTIAL	PROBABLE PROCESS C ₂ H ₆ →	CALCULATED MINIMUM ENERGY	EXCESS ENERGY OR DEDUCED I(X) (VOLTS)
C ₂ H ₆ ⁺	100	11.6 ± 0.1	C ₂ H ₆ ⁺	I(C ₂ H ₆)	I(C ₂ H ₆) = 11.6
C ₂ H ₅ ⁺	76	12.7 ± 0.2	C ₂ H ₅ ⁺ + H	I(C ₂ H ₅) + 2.9	I(C ₂ H ₅) ≤ 9.8
C ₂ H ₄ ⁺	360	12.1 ± 0.1	C ₂ H ₄ ⁺ + H ₂	12.1	W(C ₂ H ₄ ⁺) = 0
C ₂ H ₃ ⁺	105	15.2 ± 0.3	C ₂ H ₃ ⁺ + H ₂ + H	I(C ₂ H ₃) + 4.4	I(C ₂ H ₃) ≤ 10.8
C ₂ H ₂ ⁺	62	15.0 ± 0.3	C ₂ H ₂ ⁺ + 2H ₂	14.5	W(C ₂ H ₂ ⁺) = 0.5
C ₂ H ⁺	12	27.0 ± 1.0	C ₂ H ⁺ + H ₂ + 3H	I(C ₂ H) + 11.2	I(C ₂ H) ≤ 15.8
			C ₂ H ⁺ + 5H	I(C ₂ H) + 15.7	I(C ₂ H) ≤ 11.3
C ₂ ⁺	2.5	31.5 ± 1.0	C ₂ ⁺ + H ₂ + 4H	31.5	W(C ₂ ⁺) = 0
CH ₃ ⁺	9	14.2 ± 0.3	CH ₃ ⁺ + CH ₃	I(CH ₃) + 3.8	I(CH ₃) ≤ 10.4
CH ₂ ⁺	6	16.2 ± 1.0			
CH ⁺	2.5	24.5 ± 1.0			
C ⁺	1	30.4 ± 1.5			
C ₂ H ₆ ⁺⁺	1	32.0 ± 1.5			
C ₂ H ₃ ⁺⁺	.1				
H ₃ ⁺	.5				
H ₂ ⁺	5.	28.0 ± 1.5			
		31.5 ± 1.5			
H ⁺	50.	20.8 ± 1.0			
H ⁻					

* Because of the great number of possibilities to be considered together with the larger uncertainty in the measured value of the appearance potential, an attempt at further interpretation does not seem to be worth while at present.

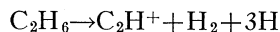
$W(\text{C}_2\text{H}_3^+)$ involved, or $I(\text{C}_2\text{H}_3)$ is actually about 11.0 volts. The second possibility appears more probable.

C_2H_2^+ . From the work of Tate, Smith and Vaughn⁹ on C_2H_2 it is known that $I(\text{C}_2\text{H}_2) = 11.2 \pm 0.1$ volts (a value in good agreement with Mulliken's spectroscopic value⁷). There are three possibilities here, but the only one that can occur at an energy low enough to agree with the observed $A(\text{C}_2\text{H}_2^+) = 15.0 \pm 0.3$ volts is

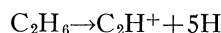


which can appear at $11.2 + 3.3 = 14.5$ volts. This means that $W(\text{C}_2\text{H}_2^+) = 0.5$ volts which is of the same order of magnitude as the probable error.

C_2H^+ . This ion was observed at $A(\text{C}_2\text{H}^+) = 27.0 \pm 1.0$ volts. K, H and T found in their interpretation of C_2H_2 that $I(\text{C}_2\text{H}) \leq 14.3$ volts and in C_2H_4 that $I(\text{C}_2\text{H}) \leq 13.8$ volts. This probably eliminates one of the three possibilities as demanding too great an amount of energy $W(\text{C}_2\text{H}^+)$ to be associated with the process. The process

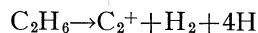


leads to a value $I(\text{C}_2\text{H}) \leq 27.0 - 11.2 = 15.8$ volts. For agreement with K, H and T this means that $W(\text{C}_2\text{H}^+) \geq 2$ volts. The reaction



means that $I(\text{C}_2\text{H}) \leq 11.3$ volts.

C_2^+ . Although there are now four possibilities to be considered, the solution appears to be unique. K, H and T found that $I(\text{C}_2^+) \leq 16.5$ volts. In the reaction



if $I(\text{C}_2^+)$ is taken as 16.5 volts, then the calculated minimum energy is 31.5 volts, agreeing with the observed appearance potential $A(\text{C}_2^+) = 31.5 \pm 1.0$ volts. Of the other three possibilities, one cannot occur at a potential this low and the other two would require that $W(\text{C}_2^+) \geq 4.4$ volts.

CH_3 . In this case the explanation of the appearance potential $A(\text{CH}_3^+) = 14.2 \pm 0.3$ volts seems to be the lowest energy process



⁹ Tate, Smith and Vaughn, Phys. Rev. **48**, 523 (1935).

From the relation

$$I(\text{CH}_3^+) + 3.8 + W(\text{CH}_3^+) = 14.2 \text{ volts}$$

the ionization potential is

$$I(\text{CH}_3) \leq 10.4 \text{ volts.}$$

This is to be compared with Smith's result from methane of $I(\text{CH}_3) \leq 9.9$ volts. Fraser and Jewett¹⁰ obtained the value $I(\text{CH}_3) = 11.1 \pm 0.5$ volts by direct measurement on free CH_3 radicals and Mulliken¹¹ made a theoretical estimate of 8.5 volts for this ionization potential. Any of the other processes would lead to $I(\text{CH}_3) < 7.8$ volts and hence do not appear to be as consistent with these values as the reaction given above.

It does not seem significant to carry the detailed analysis beyond this point due to the number of possibilities which must be considered. The complexities of the analysis suggest that a careful study of the lower mass region would be unwarranted at present.

There is one very interesting fact to be noticed in regard to the analyses of C_2H_2 , C_2H_4 and C_2H_6 : in the first molecule only the atomic hydrogen ion was observed; in C_2H_4 , both H^+ and H_2^+ were found; and finally in C_2H_6 , it was discovered that H^+ , H_2^+ and H_3^+ were all present. This is in agreement with the results that might be expected from the known structure of these molecules.

In the work of this nature there are two confusing points that need some further discussion. The first of these is concerned with the abundance of the hydrogen ions relative to the heavier masses. This quantity has been found to vary in different apparatuses in spite of the fact that the measurements in the upper mass region check rather well. For example, in the preliminary work done at Princeton on CH_4 ¹² the yield of hydrogen ions was found to be very small. Later Smith, using an apparatus of the same type but with increased sensitivity, found these ions to be rather abundant. Since, in this study of ethane, the hydrogen ions were found to be much more abundant than in any previous studies of hydrocarbons, a check was made on

¹⁰ Fraser and Jewett, Phys. Rev. **50**, 1091 (1936).

¹¹ Mulliken, J. Chem. Phys. **1**, 492 (1933).

¹² Hipple and Bleakney, Phys. Rev. **47**, 802(A) (1935).

the measurements by putting methane into this new apparatus; it was found that there was a relative increase of almost a factor of ten compared with Smith's measurements. This last increase can be partially explained by the fact that, because of the focusing properties of the new instrument, ions formed with kinetic energy will no longer cause a broadening of the main peak as in the case of magnetic focusing alone. When 75-volt electrons are used there must certainly be a great number of hydrogen ions formed with kinetic energy. However, the discrepancy existing when the two instruments are of the same type indicates that no great faith should be placed in the observed values in any event when there is so great a difference in mass. This is probably explained by a differential selection of the ions as they are accelerated from the ionization chamber into the analyzer. This last effect would of course vary with the geometrical conditions. It is due to a difference in the amount of kinetic energy associated with the formation of the ions as well as a difference in mass. Thus, if the accelerating slits in the ion gun are wide, the solid angle subtended with reference to the region in which the ions are formed will be correspondingly large; and this in turn means that a greater fraction of the ions formed with kinetic energy will enter the analyzer.

The second point that requires some dis-

cussion is the error given in the measured value of the appearance potential. Smith found that, if the conditions were varied over an extremely wide range, the uncertainty in the observed value of the appearance potential was somewhat increased; this is due to the difference in the shape of the initial portion of the molecular ionization curve as compared with that of the inert gas used for calibration. As a result, Smith was liberal in his estimate of the probable error. Certainly, under similar experimental conditions, the variation in successive measurements is much less than the errors he gives. Also the difference in the appearance potentials of the various ions is known to a greater accuracy than would be concluded from Smith's results. K, H and T evidently estimated their probable error from the internal consistency of the data taken under similar experimental conditions; since the results here given for ethane fit in so nicely with their results on ethylene, the same method of estimating the error in the measured appearance potential has been employed here.

The author is indebted to Mr. Morikawa formerly of the chemistry department for the preparation of the gas.¹³ The author also wishes to express his grateful appreciation to Professor Walker Bleakney for the supervision of this work.

¹³ Benedict, Morikawa, Barnes and Taylor, *J. Chem. Phys.* **5**, 1 (1937).