

Dissociation of Propane, Propylene and Allene by Electron Impact

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The appearance potentials of all the ions from $C_3H_3^+$ to $C_3H_2^+$ and $C_2H_5^+$ to $C_2H_2^+$ that result from the bombardment of propane, propylene and allene have been measured. Although little is known concerning the energies of the various free radicals formed, it is still possible to specify uniquely most of the reactions which lead to the observed ions. This knowledge in turn allows upper limits to be placed on the ionization potentials of the free radicals themselves. These limits range from about 9 to 12 volts, showing that the ionization potentials of these radicals do not differ greatly from one another.

IN recent years the mass spectrograph has been used with some success in the study of the dissociation of molecules when subjected to bombardment by charged particles. In the case of the simple hydrocarbons such as methane,¹ acetylene,² ethylene,³ and ethane⁴ measurements of the appearance potentials and the probabilities of ionization have thrown some light on the manner in which these molecules may be broken up into many fragments. It is the purpose of this communication to describe an extension of these investigations to a few of the hydrocarbons containing three carbon atoms, in particular propane C_3H_8 , propylene C_3H_6 , and allene C_3H_4 . Propane has already been investigated by Stewart and Olson⁵ and they found that this compound dissociated to give many types of ions, but they gave no indication of the energies involved.

The mass spectrograph used in the present investigation has been described by Bleakney and Hipple⁶ in a recent communication. The magnetic field available for this instrument was rather small (1000 gauss), and consequently the velocities of the heavier ions were not high. This means that intense ion beams cannot be used because of space charge limitations. As a result the ionization potentials were not determined with high accuracy, but on the other

hand for such interpretation as can be made high accuracy is not needed. Some of the gases studied in this research were prepared by our colleagues in the Chemistry Department, and we are much indebted to them for their courtesy. The results indicate that contaminations were extremely small.

The procedure need not be repeated here in detail since it has often been given in previous papers of this character. It will merely be recalled that the observations are carried out at very low pressure as the gas flows through the apparatus so that all the products occur as the result of single electron impacts on the normal molecule of the gas in question. In Fig. 1 is shown a "mass-spectrum" of the upper mass region for propylene. This is an actual reproduction of a run traced out by an automatic recorder obtained by varying the analyzing field (abscissa) while the detector system measures the current or intensity (ordinate). The mass 44 peak in this picture is an impurity, probably propane and CO_2 . Mass 43 contains some impurity but is largely accounted for by the C^{13} isotope. The appearance potential for the formation of each of these ions is obtained by setting the analyzer on a particular peak and recording its intensity as a function of the electron energy. The minimum electron energy necessary to form the ion is compared with that of a gas which is well known, such as argon, and in this way only differences need be measured.

A summary of the types of ions observed and their relative abundances for the three gases propane, propylene, and allene is given in Table I. In each gas the complete molecular ion is

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

² Tate, Smith and Vaughn, *Phys. Rev.* **48**, 523 (1935).

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

⁴ J. A. Hipple, *Phys. Rev.* **53**, 530 (1938).

⁵ H. R. Stewart and A. R. Olson, *J. Am. Chem. Soc.* **53**, 1236 (1931).

⁶ W. Bleakney and J. A. Hipple, *Phys. Rev.* **53**, 521 (1938).

assigned the arbitrary intensity value 100, and the others are given on this scale. These are actually observed values for electrons of 100 volts energy, and no attempt has been made to correct them for the overlapping of the carbon isotopes. Hydrogen ions are also formed in these gases, but their relative abundance was not measured. No search was made for negative ions. Appearance potential measurements were not made for the complete mass-spectrum first because of lack of time and second because of the difficulty of attaching any meaning to many of them.

The relative probabilities of formation of ions in these compounds present some interesting and peculiar features. Chemical evidence indicates the following structures: allene $\text{CH}_2 : \text{C} : \text{CH}_2$; propylene $\text{CH}_2 : \text{CH} \cdot \text{CH}_3$; propane $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_3$. It will be noticed from Table I that in propylene mass 27 is about thirteen times as strong as 28. This observation is probably to be correlated with the relative energy necessary to break a single C—C bond as compared to the double C=C bond. An unexpected peculiarity is found in the occurrence of C_2H_3^+ and CH_3^+ in allene. One possible, though improbable,

TABLE I. *The ions observed and their relative intensities as measured by the heights of the peaks.*

ION	PROPANE (C_3H_8)	PROPYLENE (C_3H_6)	ALLENE (C_3H_4)
C_3H_8^+	100		
C_3H_7^+	67		
C_3H_6^+	12.4	100	
C_3H_5^+	36	148	
C_3H_4^+	6.2	50	100
C_3H_3^+	85	85	94
C_3H_2^+	14	18.5	40
C_3H^+	8.7	12.7	30
C_2^+	1.2	2.7	9
C_2H_5^+	140	0	
C_2H_4^+	90	5	0
C_2H_3^+	52	65	5.2
C_2H_2^+	24.5	20	5.8
C_2H^+	5.4	4.6	4.2
C_2^+	0.5	1.5	2.2
$\text{C}_3\text{H}_8^{++}$	0.1		
$\text{C}_3\text{H}_7^{++}$	0		
$\text{C}_3\text{H}_6^{++}$	0.1	0	
$\text{C}_3\text{H}_5^{++}$	0.4	1.1	
$\text{C}_3\text{H}_4^{++}$	3.2	4.3	2.7
$\text{C}_3\text{H}_3^{++}$	3.2	3.2	2.7
$\text{C}_3\text{H}_2^{++}$	3.6	6.5	2.5
C_3H^{++}	0	0	0
CH_3^+	12.6	1.4	0.9
CH_2^+	6.2	7.1	3.8
CH^+	2	3.8	2.7
C^+	0.8	4.1	2.7

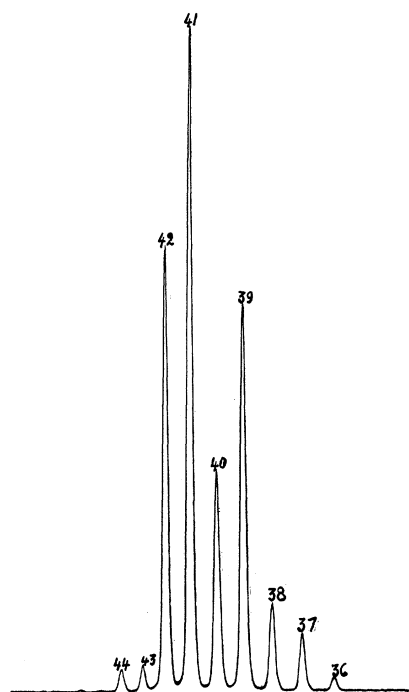


FIG. 1. Mass spectrum in the C_3 region of propylene. Energy of the bombarding electrons about 100 volts.

explanation for such ions is the presence as an impurity of methylacetylene, an isomer of allene with a CH_3 radical on one end. Another peculiar distribution of intensities is the small yield of the propylene and allene ions C_3H_6^+ and C_3H_4^+ coming from propane and C_3H_4^+ from propylene. Since these ions correspond to stable compounds, it might be supposed that they should be among the most abundant. No explanation of this behavior is known. Perhaps the ions with an even number of electrons are more stable than those with an odd number.

Before one can make comparisons of the ionization potentials with thermochemical data it is necessary to estimate the various heats of dissociation involved. The energies of the possible states in which three carbons and eight, six, and four hydrogens can exist are shown in Table II. Only the states c_1 , e_1 , and e_2 are known with any accuracy, the others being correct only in first approximation. The energies are measured from the normal state of the complete molecule in each case. States c_1 , e_1 , and e_2 have been deduced from the heat of hydrogenation of

TABLE II. *Energies of dissociation of propane, propylene and allene into their various constituents.*

PROPANE		PROPYLENE		ALLENE	
CONFIGURATION	ENERGY	CONFIGURATION	ENERGY	CONFIGURATION	ENERGY
(a ₁) C ₃ H ₈	0				
(b ₁) C ₃ H ₇ +H	2.85	(c ₂) C ₃ H ₆	0	(e ₃) C ₃ H ₄	0
(c ₁) C ₃ H ₆ +2H	5.7	(d ₂) C ₃ H ₅ +H	3.15	(f ₃) C ₃ H ₃ +H	3.75
(d ₁) C ₃ H ₅ +3H	8.8	(e ₂) C ₃ H ₄ +2H	6.3	(g ₃) C ₃ H ₂ +2H	7.5
(e ₁) C ₃ H ₄ +4H	12.0	(f ₂) C ₃ H ₃ +3H	10.0		
(f ₁) C ₃ H ₃ +5H	15.7	(g ₂) C ₃ H ₂ +4H	13.8		
(g ₁) C ₃ H ₂ +6H	19.5	(h ₂)			
(h ₁) C ₂ H ₅ +CH ₃	2.5	(i ₂)			
(i ₁) C ₂ H ₄ +CH ₄	4.0	(j ₂) C ₂ H ₃ +CH ₃	2.8		
(j ₁) C ₂ H ₃ +CH ₄ +H	0.9				
(k ₁) C ₂ H ₂ +CH ₃ +H ₂	4.0	(k ₂) C ₂ H ₂ +CH ₄	1.6	(l ₃) 3C+4H	23.2
(l ₁) C ₂ H ₂ +CH ₄ +H ₂	2.8	(l ₂) 3C+6H	29.5		
(m ₁) 3C+8H	35.2				

propylene and allene⁷ and l_1 and l_2 from the heat of combustion⁸ of propane and propylene. States b_1 and d_2 were simply estimated by interpolation and d_1 was deduced from them. A comparison between the states b_1 , c_1 , d_1 , e_1 in propane and the following ones in ethane⁴ C₂H₅+H, C₂H₄+2H, C₂H₃+3H, C₂H₂+4H, shows that the removal of one, two, three or four hydrogens requires approximately the same energy in both cases. It will be assumed that the removal of five and six hydrogens require the same energy as in ethane and so the states f_1 and g_1 are determined and f_2 , g_2 , f_3 and g_3 are easily calculated from them. The states h_1 , i_1 , j_1 , k_1 , j_2 and k_2 are independent of these assumptions and are deduced only from l_1 , l_2 , l_3 and those of ethane,⁴ ethylene,³ acetylene and methane.¹

The observations on the appearance potentials and the conclusions which may be drawn from them are summarized in Table III. The following notation has been used: X = a molecule or free

⁷ Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 876 (1935); **58**, 146 (1936).

⁸ International Critical Tables (McGraw-Hill), and F. R. Bichowsky and F. D. Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1936).

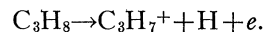
radical, $A(X^+)$ = appearance potential or minimum energy required to produce the ion X^+ from the parent molecule, $I(X)$ = ionization potential of X , $W(X)$ = excess energy (excitation + kinetic).

In column 1 of Table III are listed some of the important ions observed in the gases studied. The observed appearance potentials in the three gases are given in columns 2, 3 and 4. The processes which best account for these ions are listed in columns 5, 6 and 7. On the basis of the assignment given for each process one may calculate a value for $W(X)+I(X)$ for the free radical X . Only an upper limit can be specified for $I(X)$ because the amount of energy $W(X)$ which goes into excitation of the products or into kinetic energy of translation is unknown. This unknown energy is usually quite small, however, as shown by the agreement in $I(X)$ obtained from the different molecules. The procedure, therefore, is to assume a process of dissociation consistent with the $A(X^+)$ and the energies listed in Table II. In spite of the uncertainties involved in the data this choice is very often unique. The values of $I(X)+W(X)$ are then easily obtained by subtracting from $A(X^+)$ the energy required for dissociation as given in Table II. The data in the last three columns were taken from other papers.²⁻⁴

A discussion will now be given of some particular cases.

C₃H₇⁺

There is only one possible choice of reaction leading to this ion.



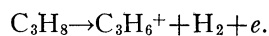
The conclusion is that $I(C_3H_7) \leq 9$ volts, but of course b_1 of Table II is not well known.

TABLE III. *Summary of the appearance potentials and the interpretations which may be made.*

X ⁺	A(X ⁺) (VOLTS)			C ₃ H ₈ →	REACTION C ₃ H ₆ →	C ₃ H ₄ →	I(X)+W(X) = UPPER LIMIT OF I(X)							
	PROPANE	PROPYLENE	ALLENE				C ₃ H ₈	C ₃ H ₆	C ₃ H ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂		
C ₃ H ₈ ⁺	11.3±0.3						11.3							
C ₃ H ₇ ⁺	11.9±0.2			C ₃ H ₇ ⁺ +H			9.0							
C ₃ H ₆ ⁺	12.3±0.3			C ₃ H ₆ ⁺ +H ₂			11.1	10.0						
C ₃ H ₅ ⁺	14.0±0.3	10.0±0.2		C ₃ H ₅ ⁺ +H ₂ +H	C ₃ H ₆ ⁺ +H		9.7	8.7						
C ₃ H ₄ ⁺	14.7±1.0	12.4±0.3	9.9±0.2	C ₃ H ₄ ⁺ +2H ₂	C ₃ H ₄ ⁺ +H ₂		11.7	10.6	9.9					
C ₃ H ₃ ⁺	15.7±0.5	14.1±0.2	12.5±0.2	C ₃ H ₃ ⁺ +2H ₂ +H	C ₃ H ₃ ⁺ +H ₂ +H	C ₃ H ₃ ⁺ +H	9.0	8.7	8.8					
C ₃ H ₂ ⁺		15.0±1.0	14.1±0.2		C ₃ H ₂ ⁺ +2H ₂	C ₃ H ₂ ⁺ +H ₂		10.2	11.2					
C ₂ H ₅ ⁺	12.3±0.2			C ₂ H ₅ ⁺ +CH ₃			9.8			9.8				
C ₂ H ₄ ⁺	12.2±0.2			C ₂ H ₄ ⁺ +CH ₄			11.3			10.8	10.8			
C ₂ H ₃ ⁺	15.2±0.3	14.5±0.3		{ C ₂ H ₃ ⁺ +CH ₄ +H C ₂ H ₃ ⁺ +CH ₃ +H ₂	C ₂ H ₃ ⁺ +CH ₃		11.2	11.7		10.8	11.0			
C ₂ H ₂ ⁺	14.4±0.5	14.0±0.5		C ₂ H ₂ ⁺ +CH ₄ +H ₂	C ₂ H ₂ ⁺ +CH ₄		11.6	12.4		11.7	11.9	11.2		

C₃H₆⁺

The observed $I(\text{C}_3\text{H}_6)$ in propylene is 10 volts. Hence from $c_1 \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6^+ + 2\text{H} + e$ will require at least 15.7 volts. The observed $A(\text{C}_3\text{H}_6^+)$ in propane is below this value and the only possible reaction is therefore



Allowing 4.5 volts for the heat of dissociation of hydrogen $I(\text{C}_3\text{H}_6) \leq 11.1$ volts. This indicates that in this case the total excess energy is about one volt.

C₃H₅⁺

The way in which this ion is obtained in propylene is unambiguous, giving an upper limit for $I(\text{C}_3\text{H}_5)$ of 8.7 volts. Once this limit is established, only one possible process can be written for $A(\text{C}_3\text{H}_5^+)$ in propane requiring less energy than that observed. The results are given in Table II.

C₃H₄⁺

The ionization potential of this molecule is measured directly in allene and with this knowledge energy considerations determine uniquely the processes responsible for its formation in propylene and propane. It is seen that the hydrogens must come off in molecular form.

C₃H₃⁺

There are two possible choices for the explanation of this ion in allene. One yields 2H and the other H₂. The second is believed to be the correct one because the other indicates an unusually high value for $I(\text{C}_3\text{H}_2)$. The same reasoning holds for the assignment in propylene.

C₃H₂⁺

The process responsible for this ion is unique in allene and the others follow on arguments similar to those given in previous cases.

C₂H₅⁺

In the formation of this ion and those that follow in the table bonds between carbon atoms must be broken. One would guess from the structure of propane that the easiest way to produce C₂H₅⁺ would be to ionize the molecule and knock a CH₃ off one end. Energy considera-

tions from Table II indicate that this is the only possible process without ascribing an abnormally low value to $I(\text{C}_2\text{H}_5)$. Moreover the upper limit deduced on this hypothesis for $I(\text{C}_2\text{H}_5)$ agrees very nicely with a similar value found in ethane⁴ and with the result given by Fraser and Jewitt.⁹

C₂H₄⁺

In the study of ethylene Kusch, Hustrulid and Tate³ found a value of 10.8 volts for the ionization potential of this molecule. There is then only one possible explanation of the appearance potential of this ion in propane and that is the formation of C₂H₄⁺ + CH₄. All other conceivable reactions require too much energy. It may seem a little surprising that this can happen as a result of a single electron impact, but there seems to be no escape from this conclusion. This point will be referred to again in the discussion at the end of this paper.

C₂H₃⁺

In propylene the simplest way to produce this ion is to remove the CH₃ radical from one end and ionize the remainder. Energetically this turns out to be a unique solution. From state j_1 of Table II it will be seen, however, that in propane there are two possibilities so nearly the same in energy that the experiments are unable to distinguish between them. Both are listed in Table III. It will be noticed that the $I(\text{C}_2\text{H}_3)$ deduced in propane and propylene agree very well with the earlier results in ethane and ethylene.

C₂H₂⁺

The ionization potential of acetylene² is 11.2 volts. The processes of formation of C₂H₂⁺ in propane and propylene are given in Table III and they are unique. It will be noticed that all the data on $I(\text{C}_2\text{H}_2)$ from various gases are in excellent agreement.

In this investigation it appears that all the ions listed in Table III are produced by that reaction which requires the least energy. This has not been true of the simpler hydrocarbons. In fact quite the opposite was true in methane¹ where the highest degree of dissociation seemed

⁹ R. G. J. Fraser and T. N. Jewitt, Phys. Rev. **50**, 1091 (1936).

to be preferred. In the two-carbon molecules^{3, 4} some hydrogen molecules were formed but not the maximum number possible. However, in propane, propylene and allene the appearance potentials correspond to the formation of the maximum number of molecules in the hydrogen which is removed. It is reasonable to suppose, however, that a molecule of hydrogen is always formed of two atoms which were originally attached to the same carbon. This hypothesis has been verified in the case of ethylene by Delfosse and Hipple.¹⁰ It will also be observed that propylene is much like ethylene except

¹⁰ J. Delfosse and J. A. Hipple, *Phys. Rev.* **54**, 1060 (1938).

that one hydrogen has been replaced by a CH₃ radical. One might expect, therefore, that CH₄ would be formed in propylene as H₂ is formed in ethylene and the experiments amply verify this hypothesis. Another example of this behavior occurs in propane where CH₄ appears in the formation of C₂H₄⁺.

The construction of the apparatus was made possible through the work of Dr. J. A. Hipple, Jr., and it is a pleasure to acknowledge this assistance as well as his help with the initial work on propane. We are greatly indebted to the Research Corporation for financial aid which has helped materially in the perfection of our apparatus.

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Collision Cross Sections for D-D Neutrons*

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The nuclear collision cross sections of 22 elements for the neutrons from a deuteron-deuteron source have been measured. The geometrical arrangement of the experiment was such that only small corrections to the measured transmission were necessary. The neutron energy was 2.88 ± 0.04 Mev. The cross sections are found to vary irregularly with the atomic weight. The proton cross

section determined for both paraffin and water scatterers is found to be 2.36×10^{-24} cm², which is smaller than the value predicted by theory. In addition, the cross sections of a number of elements for neutrons of 2.46 Mev energy have been measured. For some elements the cross section is found to increase with an increase in neutron energy, for others it decreases.

THE total collision cross section of the fast neutrons from radon plus beryllium sources for the nuclei of many of the elements of the periodic table have been measured by Dunning.¹ These cross sections when plotted as a function of the atomic weight show a slow and regular increase with atomic weight. Since, however, the neutrons from Rn+Be are highly inhomogeneous in energy, the total cross sections found with them are only averages for a considerable energy interval.

The importance in nuclear theories of neutron-proton scattering and nuclear scattering in

general makes it highly desirable to measure cross sections with neutrons of a single known energy. It is well established that the neutrons from the deuteron-deuteron reaction are, in the main, monoenergetic and hence this source has been used in a number of investigations in which such neutrons were required. Scattering cross sections for deuteron-deuteron neutrons have been measured by Booth and Hurst,² Ladenburg and Kanner,³ and recently by Kikuchi and Aoki.⁴

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¹ J. R. Dunning, *Phys. Rev.* **45**, 586 (1934).

² E. T. Booth and C. Hurst, *Proc. Roy. Soc.* **161**, 248 (1937).

³ R. Ladenburg and M. H. Kanner, *Phys. Rev.* **52**, 911 (1937).

⁴ Seishi Kikuchi and Hiroo Aoki, *Proc. Phys.-Math. Soc. Japan* **21**, 75 (1939); *Phys. Rev.* **55**, 108 (1939).