

# Radiolysis of Methane in a Wide-Range Radiolysis Source of a Mass Spectrometer. I. Individual and Total Cross Sections for the Production of Positive Ions, Negative Ions, and Free Radicals by Electrons\*

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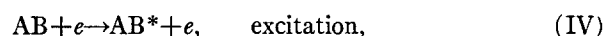
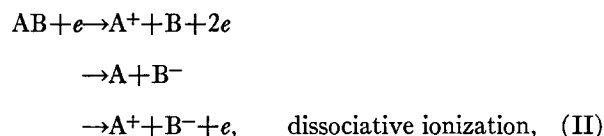
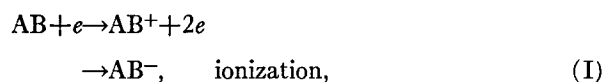
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The abundances of, and the total and individual cross sections for, primary products (positive ions, neutral species, and negative ions) resulting from elementary reactions induced by the absorption of energy by  $\text{CH}_4$  from ionizing radiation (100-eV electrons) have been measured. This was accomplished with the dual electron beam section of our wide-range radiolysis source. The results show that positive ions and free radicals are produced in nearly equal abundances, 45% and 55%, respectively. On the other hand, negative ions are less abundant by about four orders of magnitude. The total cross section for positive ionization ( $\sigma_I$ ) by 100-eV electrons is  $3.8 \times 10^{-16} \text{ cm}^2$  and that for the formation of neutral species ( $\sigma_N$ ) is  $4.7 \times 10^{-16} \text{ cm}^2$ . To independently test the reliability of the dual electron-beam ion source, the total and individual cross sections for ionization of Ar by 100-eV electrons were measured for comparison with published values. Our value for the total cross section ( $\sigma_I$ ) of  $3.24 \times 10^{-16} \text{ cm}^2$  is in satisfactory agreement with those reported by other workers, whose values range from  $(2.8 \text{ to } 3.6) \times 10^{-16} \text{ cm}^2$ .

## INTRODUCTION

It is necessary, in order to understand numerous problems in many areas of science, to have quantitative information about the abundance of primary products and the individual cross sections for reactions which lead to ionization, excitation, dissociative ionization, and dissociation of molecules induced by ionizing radiations. These types of reactions are illustrated for a typical molecule, AB, by the following notations:



where the products A and B may be either stable molecules or free radicals. For example, information about cross sections for these processes is required for the proper understanding of the elementary reactions (mechanisms) of a chemical reaction induced by the absorption of energy from ionizing radiations. Furthermore, an accurate knowledge of the dissociative-ionization cross sections is necessary for the development of a detailed collision theory and a meaningful theory of mass spectra. The data are also needed in connection with many problems in atomic and plasma physics. Thus, it is not surprising that quite a few

laboratories<sup>1-10</sup> have been studying the reactions produced by inelastic collisions of ionizing radiations with atoms, and in some cases, molecules, for many years.

The experimental measurement of the absolute value of the dissociative-ionization and dissociation cross sections is beset by exceptional difficulties. In many cases, the collection efficiency of the apparatus is not equal for the different ions because of kinetic energy and mass discrimination effects. This will be so if dissociative ionization occurs from a repulsive state. In other cases, the transitions involved may give rise to metastable ions of long lifetime so that the usual methods of measurement cannot be applied. Furthermore, cross sections for dissociation (III) and excitation (IV) are much more difficult to obtain than those for ionization (I) because of the problems involved in detecting the neutral products.

The primary purpose of the present study was to measure the absolute value of the various individual inelastic cross sections for reactions of ionizing electrons with  $\text{CH}_4$ . A number of previous investigators<sup>1-10</sup> have reported values for cross sections for total ionization of  $\text{CH}_4$ , and in two studies<sup>6,10</sup> individual cross sections for dissociative ionization. On the other hand, neither the individual nor the total cross sections for dissocia-

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<sup>8</sup> D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **43**, 1464 (1965).

<sup>9</sup> P. S. Rudolph and C. E. Melton, *J. Chem. Phys.* **45**, 2227 (1966).

<sup>10</sup> R. E. Glick and J. A. Llewellyn, *U.S. At. Energy Comm. Bulletin*, F.S.U. 2690-14 (1966).

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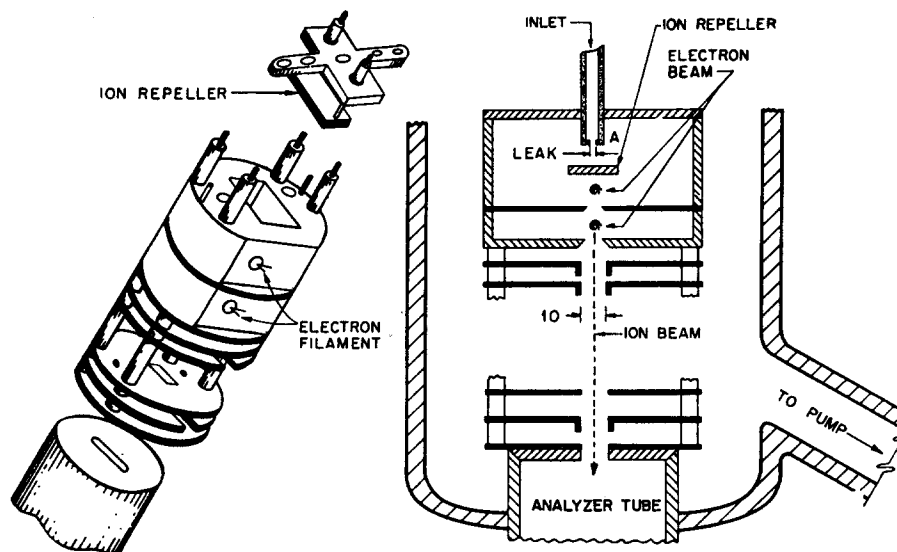


FIG. 1. Dual electron-beam ion source for the study of neutral and ionic transient species in a mass spectrometer.

### MASS SPECTROMETER ION SOURCE

tion have been reported. It is the aim of this research, which will be reported in a series of papers, to study the radiolysis of  $\text{CH}_4$  which includes a knowledge of the cross sections for the elementary reactions that ultimately lead to the final reaction products. We, therefore, began the research with an investigation of the initial processes, that is, the primary reactions resulting from the interaction of ionizing radiation with isolated molecules of  $\text{CH}_4$ .

### EXPERIMENTAL

Experimental measurements were made in the dual electron-beam section of the wide range radiolysis source,<sup>11,12</sup> Fig. 1, of our research mass spectrometer which is a 6-in. radius, 60°-sector magnetic deflection instrument. It has been suitably modified for the meas-

urement of absolute values of cross sections for ionization, dissociative ionization, excitation, and dissociation and the modifications are described in detail elsewhere.<sup>9,11,12</sup> Inelastic cross sections were obtained for an electron energy of 100 eV because this is the energy range of most interest in gas-phase radiolysis of  $\text{CH}_4$ . Cross sections for reactions of Types (I) and (II) were measured using compartment two only, whereas the measurement of individual cross sections for dissociation (III) required the use of both compartments one and two. Briefly, the dissociation cross sections were obtained by first dissociating the molecules in compartment one with an electron beam of known intensity and then measuring the abundance of the resultant neutral products by ionizing them in compartment two. Values were obtained from the relationship<sup>11</sup>

$$A^+ = \sigma \cdot \sigma_i [A] N_e N_e' W' \eta / V \quad (1)$$

TABLE I. Individual cross sections for initial products produced by the irradiation of  $\text{CH}_4$  with 100-eV electrons at a pressure of  $6 \times 10^{-6}$  torr.

Positive ions			Neutral species			Negative ions		
Ion	% of total products	$\sigma \times 10^{16}$ (cm <sup>2</sup> )	Neutral	% of total products	$\sigma \times 10^{16}$ <sup>a</sup> (cm <sup>2</sup> )	Ion	% of total products	$\sigma \times 10^{21}$ (cm <sup>2</sup> )
$\text{H}^+$	0.47	0.04	$\cdot\text{H}$	28.24	2.4	$\text{H}^-$	$8.242 \times 10^{-4}$	8
$\text{H}_2^+$	0.24	0.02	$\text{H}_2$	9.41	0.8			
$\text{C}^+$	0.59	0.05	$\cdot\text{C}$	0.001	...	$\text{C}^-$	$8.38 \times 10^{-5}$	0.81
$\text{CH}^+$	1.65	0.14	$\cdot\text{CH}$	1.18	0.1	$\text{CH}^-$	$6.6 \times 10^{-5}$	0.8
$\text{CH}_2^+$	3.29	0.28	$\cdot\text{CH}_2$	2.35	0.2	$\text{CH}_2^-$	$2.5 \times 10^{-5}$	0.24
$\text{CH}_3^+$	17.65	1.5	$\cdot\text{CH}_3$	14.12	1.2	$\text{CH}_3^-$	$9 \times 10^{-7}$	0.09
$\text{CH}_4^+$	21.18	1.8						
	45	3.8		55	4.7		$1.33 \times 10^{-3}$	9.9

<sup>a</sup> These values determined from Eq. (1) by the use of the following cross sections (in units of  $10^{-16}$  cm<sup>2</sup>) for ionization of the neutrals by 100-eV electrons; H (0.6), CH (1.1),  $\text{CH}_2$  (1.4), and  $\text{CH}_3$  (1.8).

<sup>11</sup> C. E. Melton, J. Sci. Instr. **43**, 927 (1966).

<sup>12</sup> C. E. Melton, J. Chem. Phys. **45**, 4414 (1966).

TABLE II. Individual and total cross sections for positive ionization of CH<sub>4</sub> by 100-eV electrons at a pressure of 10<sup>-6</sup> torr.

Ion	Individual cross section $\sigma_i$ in units of 10 <sup>-16</sup> (cm <sup>2</sup> )			Mass spectra			
	This study	GL <sup>a</sup>	ABSK <sup>b</sup>	This study	GL <sup>a</sup>	ABSK <sup>b</sup>	API <sup>c</sup>
CH <sub>4</sub> <sup>+</sup>	1.8	2.4	1.5	100	100	100	100
CH <sub>3</sub> <sup>+</sup>	1.5	1.8	1.3	83.33	75.00	86.67	85.9
CH <sub>2</sub> <sup>+</sup>	0.28	0.47	0.21	15.56	19.58	14.00	16.1
CH <sup>+</sup>	0.14	0.22	0.10	7.78	9.17	6.67	8.09
C <sup>+</sup>	0.05	0.07	0.04	2.78	2.92	2.67	2.80
H <sub>2</sub> <sup>+</sup>	0.02		0.02	1.11		1.33	0.21
H <sup>+</sup>	0.04		0.11	2.22		7.33	3.36
Total	3.8	5.0	3.3				

<sup>a</sup> Reference 10.<sup>b</sup> Reference 6.<sup>c</sup> Reference 16.

where  $A^+$  is the ion current from the product of interest,  $\sigma_*$  is the cross section for dissociation of a molecule into neutral products,  $\sigma_i$  is the cross section for ionization of a given neutral product,  $\eta$  is the transmission coefficient for a neutral product from compartment one to compartment two, and  $V$  is the average velocity of that neutral product,  $[A]$  is the concentration of reactant molecules (CH<sub>4</sub>) in compartment one,  $N_e$  and  $N_e'$  are the electron currents in compartments one and two, and  $l$  and  $l'$  are the corresponding electron path lengths. The path length  $l$  of the electrons is not the linear distance across the ionization chamber, but rather the distance described by a helix of radius determined by the strength of the collimating magnet  $H$  and the initial direction of the electrons with respect to the magnetic field. If  $d$  is the diameter of the electron defining aperture, and  $E$  is the energy of the electrons in electron volts, the maximum path length of an electron is given by<sup>13</sup>

$$l = l_0(1 + 1.1 \times 10^{-4} d^2 H^2 / E). \quad (2)$$

TABLE III. Experimental values for total cross section for ionization of CH<sub>4</sub> by 75–100-eV electrons.

Experimental <sup>a</sup>	CH <sub>4</sub>	
	Total cross section $\sigma_T \times 10^{16}$ (cm <sup>2</sup> )	Electron energy $E_e$ (eV)
1	2.84	75
2	4.65	75
3	3.23	75
3	3.15	100
4	2.21	100
5	2.7 <sup>b</sup>	100
6	3.2	100
7	3.9	100
8	3.66	100
10	4.5	100
This work	3.81	100

<sup>a</sup> Number refers to reference number.<sup>b</sup> Interpolated value.

<sup>13</sup> H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact* (Oxford University Press, Oxford, England, 1952), p. 34.

For our experimental conditions,  $d = 1$  mm,  $H = 250$  G, and  $E = 100$  V. The maximum path length of any of the electrons in the beam was only about 6% greater than the linear distance. The linear distance was used for the present calculations since the error involved would be much less than 6%. Equation (2) does not allow for an increase in the path length of electrons caused by elastic scattering. It has been shown<sup>3</sup> that such an increase in path length,  $\Delta l$ , is given by the relationship

$$\Delta l = \frac{1}{2} N \sigma_s l^2 (\log_e \cos \theta + \cos \theta)_{\theta=0}^{\theta=\sec^{-1} \lambda / l} + \frac{\lambda}{l} N \sigma_s \int_0^l (l-x) dx \frac{l}{\lambda}. \quad (3)$$

In this relationship  $N$  is the number of molecules per cubic centimeter,  $\sigma_s$  is the cross section for elastic scattering of electrons by the gas,  $\lambda$  is the mean free path of the electrons,  $\theta$  is the angle of deviation from the electron beam, and  $x$  is the distance traversed through the ionization chamber. Substituting parameters from our experimental conditions in Eq. (3) showed that the increase in path length (<1%) due to elastic scattering could be neglected in this study.

The cross sections for ionization  $\sigma_i$  of the free-radical products were unknown but necessary to calculate  $\sigma_*$ , Eq. (1). We, therefore, assumed the  $\sigma_i$ 's to be equal to those for similar molecules determined at an equal  $(E-I)$ , using the relationship

$$\sigma_i = \sigma_0(E-I), \quad (4)$$

where  $\sigma_0$  is a constant,  $E$  is the electron energy, and  $I$  is the corresponding ionization potential. For example,  $\sigma_i$  for ionizing CH<sub>3</sub> ( $I = 9.8$  eV)<sup>14</sup> by 13.8-eV electrons ( $E$ ) was assumed to be equal to  $\sigma_i$  for the ionization of CH<sub>4</sub> ( $I = 13.0$  eV)<sup>15</sup> by 17-eV electrons. The use of this unavoidable assumption contributed to the uncertainty in the value of the individual cross sections for dissociation,  $\sigma_*$ .

<sup>14</sup> C. E. Melton and W. H. Hamill, *J. Chem. Phys.* **41**, 3464 (1964).

<sup>15</sup> C. E. Melton and W. H. Hamill, *J. Chem. Phys.* **41**, 546 (1964).

TABLE IV. Individual and total cross sections for the ionization of argon by 100-eV electrons.

Ion	Abundance	Relative intensity	Individual cross section $\sigma \times 10^{16}$ (cm <sup>2</sup> )
Ar <sup>+</sup>	92.56	100	2.79
Ar <sup>++</sup>	7.28	15.73	0.22
Ar <sup>3+</sup>	0.16	0.52	<0.01
Total cross section			
	Previous	Reference	This work
	3.6	17	3.24
	3.6	18	
	3.6	19	
	3.5	1	
	2.8	20	

## RESULTS AND DISCUSSION

By a carefully conducted series of measurements, we have determined the individual inelastic cross sections for ionization, positive and negative dissociative ionization and dissociation [Reactions (I)–(III)] of CH<sub>4</sub> by 100-eV electrons. The results are given in Table I. An interesting feature of the results is the nearly equal abundance of positive ions (45%) and neutral species (55%).

We calculated the mass spectrum for the various ions from CH<sub>4</sub> from the individual cross sections. The results are given in Table II together with results of other workers.<sup>6,10,16</sup> The present results for individual cross sections are in good agreement with those reported by Adamczyk *et al.*<sup>6</sup> with the exception of the value for H<sup>+</sup>. In general, the present values are slightly higher than those reported by these workers. However, their value for H<sup>+</sup> is much higher than our value. This discrepancy cannot be explained on the basis of either mass discrimination or kinetic-energy effects in our apparatus. This is true because we observe higher relative abundances for other low-mass fragment ions which undoubtedly have excess kinetic energy. Furthermore, a careful study of the intensity of H<sup>+</sup> vs electric field strength in the ion chamber demonstrated that we were collecting essentially 100% of the H<sup>+</sup> ions formed. This conclusion was based on the fact that the H<sup>+</sup> intensity remained essentially constant (a maximum

deviation of 16%) over the range 400 to 1200 V/cm. Thus, we are at a loss to explain the difference.

In Table III we present experimental results for the total cross section for comparison with those reported by other workers.<sup>1–8,10</sup> Our values are obtained by a summation of the individual cross sections. From Table III, it can be seen that the reported values for the total ionization cross section for CH<sub>4</sub> range from 2.2 to 4.7  $\times 10^{-16}$  cm<sup>2</sup>. Consequently, a comparison of the present values with those previously reported does not give an adequate test of their accuracy. We, therefore, determined the total ionization cross section for Ar to test the reliability of our method. The results are given in Table IV for comparison with those reported by other workers.<sup>17–20</sup> Satisfactory agreement between the present results and those of other investigators indicates the present techniques are reliable.

The referee pointed out that the experimental value for the total cross section for production of a given neutral should exceed the summation of specific cross sections which also give the neutral. Thus, for  $\sigma(\cdot\text{H})$  one writes the inequality

$$\sigma(\cdot\text{H}) > \sigma(\text{CH}_3^+) + \sigma(\cdot\text{CH}_3) + \sigma(\text{CH}^+) + \sigma(\cdot\text{CH}).$$

Substituting values from Table I in the above inequality, we find  $\sigma(\cdot\text{H}) > 2.9 \times 10^{-16}$  cm<sup>2</sup>, whereas the experimental value is  $2.4 \times 10^{-16}$  cm<sup>2</sup>, significantly lower than that expected on the basis of the inequality. There are several possible explanations for this discrepancy. First, should the  $\cdot\text{H}$  atoms be produced with excess kinetic energy, the value of  $V$  for Eq. (1) would be much higher than thermal conditions dictate and hence would give a low experimental value. Second, loss of  $\cdot\text{H}$  atoms by reactions could lower the cross section. This explanation appears unlikely for the pressure used in the determination. Third, the ionization efficiency curve for  $\cdot\text{H}$  was assumed to be identical in shape to that for H<sub>2</sub> with  $\sigma(\cdot\text{H}) = \frac{1}{2}\sigma(\text{H}_2)$  over the energy range of interest. This assumption is probably reasonable. We, therefore, conclude that the apparently low experimental value results from excess kinetic energy of the neutral fragments.

<sup>17</sup> P. T. Smith, Phys. Rev. **36**, 1293 (1930).

<sup>18</sup> W. Bleakney, Phys. Rev. **36**, 1303 (1930). (1960).

<sup>19</sup> B. A. Tozer and J. D. Craggs, J. Electron. Control **8**, 103 (1960).

<sup>20</sup> B. L. Schram, H. R. Moustafa, J. Schutten, and F. J. De Heer, Physica **32**, 734 (1966).

<sup>16</sup> American Petroleum Institute Research Project 44 "Catalog of Mass Spectral Data" (Carnegie Institute of Technology, Pittsburgh, Pa., 1947), Serial No. 1.