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The Effect of Electric Fields on the Decomposition of Ethane by Alpha-Rays

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In the decomposition of ethane by alpha-rays the reaction is largely initiated by splitting of molecules on ionization and by splitting of molecules without ionization on electron collision. The application of even a weak electric field results in an increased ion yield in ethane, a phenomenon which has not been observed in other gases studied by this method, and this is attributed to inhibition by the field of a reaction involving ions which decreases the amount of non-condensed gas produced. The application of higher fields results in another increase in the ion yield due to the collisions of electrons accelerated by the field which cause splitting with or without attachment. At the lower pressure, a final constancy of the ion yield at high fields can be attributed to the final attachment of all of the free electrons to molecular fragments. The reaction at the higher pressure was not followed to sufficiently high values of X/p to exhibit the same high field effect.

THE experimental procedure of this work followed that described in a recent paper¹ by the authors on the alpha-ray decomposition of nitrous oxide, the principal change being that liquid nitrogen instead of liquid oxygen was used to condense out the ethane when measuring the pressure of non-condensed gaseous products because of the higher vapor pressure of ethane at low temperatures. The ethane was obtained from a cylinder supplied by the Ohio Chemical Company and was purified by passing through solutions of ammoniacal cuprous chloride, sulfuric acid, bromine water, and potassium hydroxide, followed by drying over anhydrous calcium chloride. The gas was further purified by fractional distillation from liquid oxygen, the first and last fractions being discarded in each of four successive distillations. The purified gas was then transferred to the reaction system at the desired pressure.

The decomposition of ethane by alpha-rays has been studied by Mund and Koch² who observed the formation of liquid products and of a gaseous product which was not condensed by liquid air. Lind and Bardwell³ have also investigated the reaction and they also observed the formation of liquid products of formula $C_nH_{1.85n}$, as well as hydrogen, methane, propane, butane, and pentane, but no ethylene. The latter authors found that 1.7 molecules of ethane were decomposed per ion pair, or 1.5 molecules of hydrogen plus methane were produced per ion pair, about five molecules of hydrogen being obtained for each molecule of methane. In both of these studies the fraction of the ethane decomposed was much larger than that reported in the present work. No chemical analysis of the products was made in the present work. The reaction was followed by measuring the pressure of the gaseous products which were not condensed by liquid nitrogen, i.e., hydrogen and methane.

The results are listed in Table I and are shown graphically in Fig. 1. The ion yield as given here is the number

of molecules of non-condensed gaseous products produced per ion pair. It should be noted that even the highest field strength employed was below the value required to produce ionization by collision due to the field, as is apparent from the appearance of the current-potential curve. The ion yield curve at 200 mm was not investigated at as high a value of X/p as at 85 mm because the higher voltage required in the former case caused electrical difficulties.

DISCUSSION

The most unusual feature of the ion yield— X/p curve for ethane—is the initial rise in ion yield with increased field strength. This is the first time that this phenomenon has been observed. Its probable significance will be discussed later.

After the initial rise followed by a horizontal section, above an X/p value of approximately 6 volts/cm/mm C_2H_6 , the ion yield again increases and this is evidently the phenomenon generally observed, namely, the onset

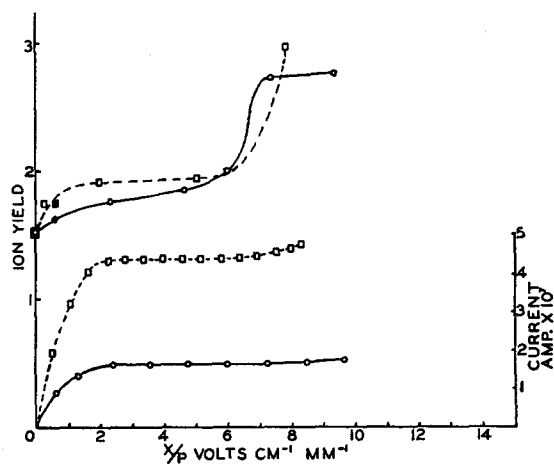


FIG. 1. The two upper curves show the variations in ion yield with X/p , the dashed curve at 200 mm, the solid curve at 85 mm pressure. Values of ion yield at fields sufficient to give half-saturation currents are indicated by solid points. The two lower curves are typical current — X/p curves at 200 mm (dashed line) and 85 mm (solid line), respectively.

* Du Pont Fellow, 1947–48.

¹ N. T. Williams and H. Essex, *J. Chem. Phys.* **16**, 1153 (1948).

² W. Mund and W. Koch, *Bull. soc. chim. Belg.* **34**, 119 (1925).

³ S. C. Lind and D. C. Bardwell, *J. Am. Chem. Soc.* **48**, 2335 (1926).

TABLE I. Ethane decomposition. Ion yields at 200 mm pressure and 21°C.

X/p	Duration of run in hours	Increase of pressure of non-condensed gases in mm	Saturation current amp. $\times 10^7$	Ion yield
0	267.33	0.1369	4.30	1.47
0	186.25	0.0978	4.37	1.49
0	182.50	0.0924	4.32	1.45
0	251.25	0.1447	4.41	1.61
0	208.50	0.1189	4.41	1.60
0	208.00	0.1177	4.25	1.65
		average		1.54
0.2*	433.00	0.2725	4.38	1.77
0.2*	161.75	0.1002	4.41	1.74
		average		1.76
0.6**	185.67	0.1123	4.37	1.71
0.6**	279.20	0.1748	4.36	1.77
0.6**	162.50	0.1064	4.42	1.83
0.6**	234.50	0.1423	4.40	1.71
0.6**	161.00	0.0922	4.24	1.67
		average		1.74
2.0	185.75	0.1293	4.36	1.97
2.0	186.50	0.1227	4.26	1.91
2.0	183.25	0.1200	4.26	1.90
		average		1.93
5.1	212.55	0.1532	4.48	1.99
5.1	160.50	0.1067	4.25	1.93
		average		1.96
7.9	144.00	0.1590	4.59	2.98
Ion yields at 85 mm pressure and 21°C.				
0	377.25	0.0798	1.69	1.55
0	259.75	0.0533	1.69	1.50
		average		1.53
0.6**	237.50	0.0521	1.68	1.61
0.6**	210.00	0.0470	1.69	1.64
		average		1.63
2.3	200.75	0.0485	1.69	1.77
4.7	190.25	0.0480	1.68	1.86
6.1	241.75	0.0665	1.68	2.02
7.5	240.00	0.0899	1.70	2.72
9.4	253.75	0.1023	1.80	2.77

* X/p values at quarter-saturation current.** X/p values at half-saturation current.

of a reaction initiated by more severe electron collisions with molecules. Data on electron energies in ethane as a function of X/p are not available, but maximum energies may be calculated roughly using the kinetic theory equation for the terminal energy E_t of an electron in a gas as a function of X/p in which only elastic collisions are assumed.⁴ This equation may be stated in the form

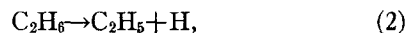
$$E_t = k((M/m)^{1/2}/\sigma^2)(X/p),$$

where M is the mass of a molecule of the gas, m is the mass of the electron, and σ is the diameter of a molecule of the gas. Substitution of the proper numerical values in this equation shows that the terminal energy acquired by an electron at any value of X/p in nitrous

oxide is 1.9 times as great as the terminal energy the electron would acquire in ethane. The point of inflection on the ion yield curve in nitrous oxide¹ probably corresponds to the decomposition



which requires about 1.8 ev. The value of X/p at the considered point of inflection on the ethane ion yield curve (~ 6.5) is 3 or 4 times the value of X/p of the corresponding point of inflection on the N_2O curve which indicates that the reaction occurring on electron collision in ethane is one requiring about double the electron energy required for the N_2O decomposition. The energy necessary to break the first C—H bond in ethane, i.e., for the reaction



is about 4.2 ev,⁵ and the energy required to break the C—C bond in ethane, i.e., for the reaction



is about 3.7 ev.⁵ According to Faltings,⁶ the split in the photo-chemical decomposition of ethane is into two methyl radicals, and according to Steacie and Cunningham⁷ and Steacie and Potvin⁸ in the mercury- and cadmium-sensitized photo-decomposition the split is into an ethyl radical and a hydrogen atom. Presumably the decompositions (2) and/or (3) on electron collision may occur either with or without attachment of the electron to one of the fragments. The flattening off of the ion yield at high X/p values at the lower pressure may be explained, as in the case of nitrous oxide,¹ by the final attachment of all of the free electrons to molecular fragments. Apparently the ion yield at the higher pressure was not followed to sufficiently high values of X/p to exhibit the same high field strength effect.

From data in Rutherford, Chadwick, and Ellis⁹ it can be calculated that in ethane one alpha-particle expends 26.9 ev per ion pair. Therefore, as about 80 percent of the ionization is secondary,⁹ the average energy of the electrons expelled by an alpha-particle (delta-rays) is 108 ev. As most of the ionization is by electrons, the positive ions to be expected when an alpha-particle travels through ethane may be obtained from mass-spectrographic data of Hipple¹⁰ and of Stevenson and Hipple.¹¹ The paper by Stevenson and Hipple shows the effect of varying electron energy on the frequency distribution of the various positive ions, and it is interest-

⁵ E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1946), p. 79.

⁶ K. Faltings, Ber. d. D. Chem. Ges. 72B, 1207 (1939).

⁷ E. W. R. Steacie and R. L. Cunningham, J. Chem. Phys. 8, 800 (1940).

⁸ E. W. R. Steacie and R. Potvin, J. Chem. Phys. 7, 782 (1939).

⁹ Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances* (Cambridge University Press, London, 1930), pp. 81, 145.

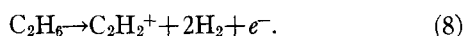
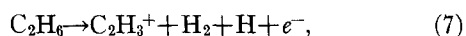
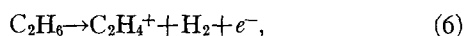
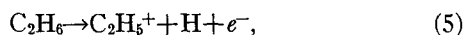
¹⁰ J. A. Hipple, Jr., Phys. Rev. 53, 530 (1938).

¹¹ D. P. Stevenson and J. A. Hipple, Jr., J. Am. Chem. Soc. 64, 1588 (1942).

⁴ L. B. Loeb, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1927), p. 501.

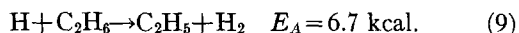
ing to note that there is little change in this distribution when the bombarding electrons have energies from 30 to 175 volts. The only negative ion reported is H⁻.

From the relative abundance of the positive ions produced in ethane on ionization by electrons the mechanism of the alpha-ray decomposition of ethane in the absence of a field may be approximately visualized. The important primary processes of ionization are:¹⁰

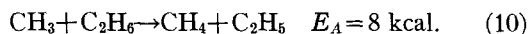


It seems probable that these, together with reactions (2) and/or (3), constitute the important primary processes which result in decomposition at no field. If we assume that the positive ions yield only products condensed by liquid nitrogen and that each H atom reacts with ethane to produce a molecule of hydrogen, then using the frequency distribution obtained by Stevenson and Hipple¹¹ we obtain 1.1 molecules of non-condensed gas per ion pair *due to the primary ionization process*. Since the ion yield obtained at no field is 1.5, it appears that 1.5 minus 1.1, or 0.4, is the ion yield due to molecule splitting, without ionization, on electron collision.

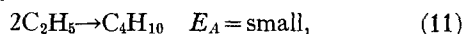
Steacie¹² has given what he considers the most reliable values for the activation energies of the possible subsequent reactions which the radicals H, CH₃, and C₂H₅ may undergo. In these experiments the most probable reactions in the gas phase are:



and



The reaction:

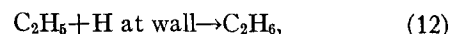


may occur to some extent in the gas phase because the ethyl radicals would not be removed by reaction with ethane molecules. Other reactions in the gas phase which involve only radicals are very improbable because of the very minute concentrations of the radicals. Faltings⁶ has explained the photo-chemical decomposition of

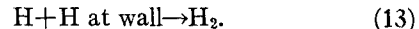
ethane by a methyl radical mechanism in which the radicals combine with each other to give the products. However, since his radical concentrations were larger than those obtained in this work by at least several powers of ten, reaction between radicals in the gas phase is much less probable here. Also at the low pressures of these experiments most of the ions should be neutralized at the wall and therefore most of the reaction between radicals in these experiments would be expected to occur on the walls.

At both pressures, the ion yield increases with the field strength as the field is increased from zero to saturation. This shows that a reaction *involving ions* which decreases the amount of non-condensed gas produced is stopped by the field. The ions C₂H₅⁺ and H⁻ have been shown in the mass-spectrograph^{10,11} studies to be produced by electron bombardment of ethane. In a field, the C₂H₅⁺ ions would be neutralized at the negative electrode yielding C₄H₁₀ and the H⁻ ions at the positive electrode yielding H₂, whereas in the absence of a field the C₂H₅⁺ and H⁻ would be neutralized at the wall and some of them would react with each other to give ethane.

The greater effect of the field at high pressure can be explained on the basis of the competing wall reactions:



and



At the lower pressure the rates of both reaction (12) and reaction (13) are slower. However, to the extent that reaction (3) with (10) is the source of C₂H₅, reaction (12) will decrease relative to (13) and correspondingly more hydrogen is produced at the wall. Consequently, on applying a field there will be a smaller increase in the hydrogen produced and a smaller increase in the ion yield (molecules of gas not condensed per ion pair). If this is the explanation of the smaller effect of the field at the low pressure, it would seem to imply a larger ion yield at no field at low pressure, whereas our measurements show no effect of pressure on the ion yield at no field. The agreement in the ion yield at the two pressures at no field may be fortuitous and due to experimental errors, but it is possible to explain such a phenomenon. It may be that at the higher pressure the production of methane by reaction (10) compensates for the increased amount of reaction (12) which takes place at this pressure.

¹² See reference 5, p. 519.