The Ionization Potentials of Formaldehyde and Halogen Derivatives of Methane

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The ionization potentials of CH_2O, CH_3Cl, CH_3Br, CH_3I were measured by a molecular ray method, and found to be 11.3, 10.7, 10.0, and 9.1 volts, respectively.

IN the course of experiments following the lines of the program laid down by Fraser[1] on the application of molecular ray methods to the study of chemical reactions, an apparatus was built which lent itself to the rapid and easy measurement of the ionization potentials of a number of organic molecules.

The molecules investigated were HCHO, CH_3Cl, CH_3Br and CH_3I. These were chosen because the analysis of their spectra is comparatively far advanced, and a determination of their first ionization potentials would furnish an independent value of the electronic series limits.

The principle of the method is as follows: When a beam of molecules is allowed to enter the space between cathode and anode of a diode, ionization begins when the filament-anode voltage is greater than the ionization potential. If now the emission is controlled by space-charge conditions, the positive ions partially neutralize the negative space-charge of the electrons, and the emission increases. Further, if the anode is made a closed cylinder the efficiency of the positive ions in neutralizing space-charge is greatly increased, since the life of the ions in the neighborhood of the cathode is lengthened.[2]

Since the actual increase in emission is of the order of a thousandth of the emission current itself, a bridge-balanced circuit was used. A second similar closed-anode diode, into which the beam did not enter, was placed in the arm of the bridge adjacent to that containing the ionizing "Kingdon cage". With this arrangement the increase of emission current on entry of the beam is read directly as a galvanometer deflection. The use of the second diode also eliminates disturbances due to stray pressure fluctuations.[3] The extrapolation of the deflection *vs.* anode voltage

curve to zero deflection gives the value of the ionization potential.

The apparatus and circuit (see Fig. 1, which is self-explanatory) were, except for a few minor improvements, the same as those used by Estermann and Stern[4] in their application of the Kingdon principle as a general method for detecting molecular beams.

The correct voltage scales were obtained by calibration with mercury, with the spectroscopic value (10.4 volts) of its ionization potential. The results are shown in Figs. 2 and 3 and in Table I.

TABLE I. *Ionization potentials.*

Substance	V_i(volts)	cm^{-1}
H·CHO	11.3±0.5	91,600
CH_3Cl	10.7±0.3	86,700
CH_3Br	10.0±0.25	81,100
CH_3I	9.1±0.25	73,800

There is of course a finite concentration of dissociation products in the cage due to decomposition at the hot filament. The corresponding stationary pressure is however certainly less than 5 percent of that of the undissociated molecules, the ratio of the stationary pressures of each dissociated product (p') and of the undissociated
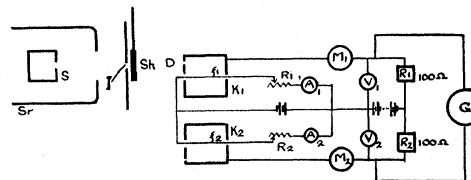

FIG. 1. Diagram of apparatus and electrical connections. *S*, Source; *I*, image aperture; *D*, entrance for beam; *Sh*, shutter; *Sr*, cooled screen; f_1, f_2, filaments; K_1, K_2, closed anodes; A_1, A_2, ammeters; M_1, M_2, milliammeters; V_1, V_2, anode voltmeters; *G*, galvanometer, $S_i = 100$.

[1] R. G. J. Fraser, Faraday Soc. Trans. **30**, 182 (1934).
[2] Kingdon, Phys. Rev. **21**, 408 (1923).
[3] Cf. Knauer and Stern, Zeits. f. Physik **53**, 766 (1929).
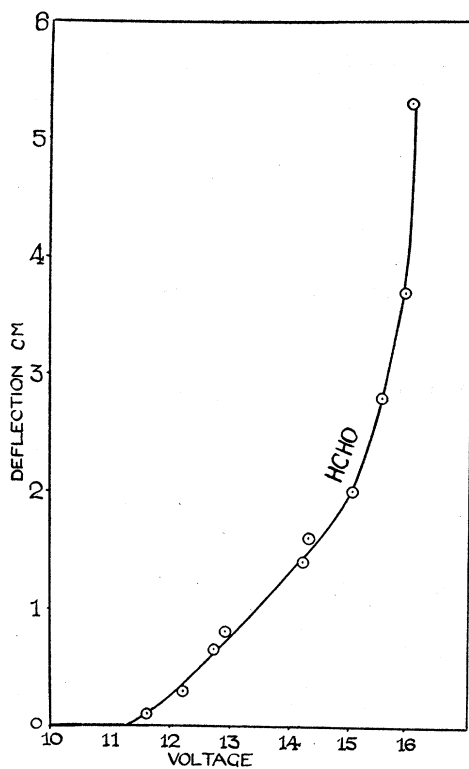[4] Estermann and Stern, Zeits. f. Physik **85**, 135 (1933).

FIG. 2. Curve showing ionization potential of formaldehyde.

FIG. 3. Curves showing ionization potentials of methyl iodide, methyl bromide and methyl chloride.

molecules (p_0) being given by

$$p'/p_0 = (T_0/T_1)^{\frac{1}{2}}(a/a') \cdot \exp E/RT,$$

where T_0 is taken to be the temperature of the walls of the cage, T_1 is the filament temperature, a, a' are the areas of filament and anode apertures, respectively, and E is the energy of activation necessary for dissociation at the filament,
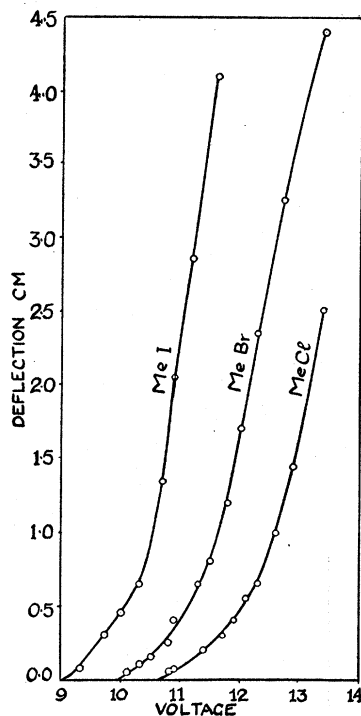
the accommodation coefficient being assumed to be unity.

Under the conditions of the experiment $T_0 = ca.$ 600°K, $T_1 = 2400$°K, $a = 6 \times 10^{-2}$ cm², $a' = 8 \times 10^{-2}$ cm². Taking $E = 10,000$ cals., $p'/p_0 = 0.045$.