Ionization Potentials of Some Organic Molecules. I. Apparatus

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With the rapid progress in the theories of molecular orbitals the study of ionization potentials of molecules has gained much theoretical importance. Besides being used to determine which electron is the most loosely bound¹⁾, they can provide data for the calculation of electronic wave functions²⁾. And recently these data have been employed even in interpreting the mechanism of organic reactivity³⁾. In spite of these facts there are available comparatively few data for only a small number of molecules. In the series of the present reports some results of our measurement will be given which have recently been carried out by the use of a mass spectrometer constructed in the laboratory of the present writers.

Instrumental Details and Experimental Method

The apparatus constructed and employed by the present writers belongs to a Hagstrum type mass spectrometer⁴⁾. Its main part of the electron and ion gun circuits is shown schematically in Fig. 1. Electrons emitted from the hot tungsten

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1) R.S. Mulliken, *Phys. Rev.*, **46**, 549 (1934); *J. Chem. Phys.*, 3, 514 (1935).

2) G.G. Hall and J.E. Lennard-Jones, *Proc. Roy. Soc.* (London), A **202**, 155 (1950); A **205**, 541 (1951).

3) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 563 (1954).

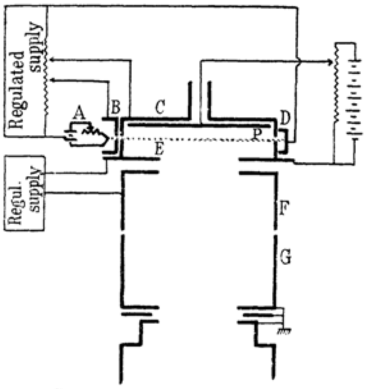

Fig. 1. Schematic diagram of electron and ion gun circuits of a mass spectrometer. A filament, B, C electron accelerating plates, C ionization chamber, D electron trap, P pusher electrode, E electron beam, F, G ion accelerating plates.

filament A are collimated into a beam by the systems of electrodes, B, C, enter the ionization chamber and finally are collected into the trap, D. The energy of the electrons causing ionization is largely determined by the potential difference between C and A, which can be varied. Ions formed in this chamber are acted on by a cross-field of up to one volt, which is applied between the pusher electrode P and the ionization chamber, and then they pass into the F—G lens in which they focus upon the input slit of the magnetic analyzer[4]. In order to make the collimation of the electron beam easier, a magnetic field of 200 oersted is applied, the lines of force of which are parallel to the axis of the electron beam.

Finally, ion currents to the collector plate are measured and their dependence on the potential difference between C and A is recorded. The latter quantity is not to be simply put as equal to the energy of the ionizing electron beam. That is, there are many complicating factors which influence the energy of the ionizing electron[5]. From among the factors examined in the present work, two will be mentioned; viz., the effects of the pusher voltage and the intensity of ion current. First, the effect arising from the pusher voltage is shown in Fig. 2. The linear relationship exists between the ionization potential and the pusher voltage which is in accord with the calculation of Jordan et al[6]. Second, Fig. 3 shows the effect due to the intensity of the electron current. The variation of the ionization potential is less pronounced in the critical slope method[7] than in the usual extrapolation method.

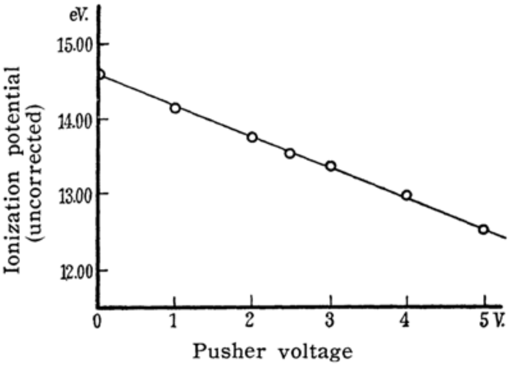

Fig. 2. Variation of the uncorrected ionization potential of argon with the potential of the cross field.

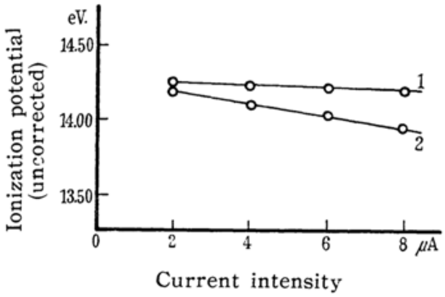

Fig. 3. Variation of the uncorrected ionization potential of argon with the intensity of the electron current.
1 critical slope method; 2 extrapolation method.

The ionization potentials recorded in the present work were determined in comparison with the spectroscopic value of argon, 15.76 eV. This standard gas is introduced and measured, immediately before and after the ion being studied. The fluctuations in this correction in a day were usually less than ±0.02 eV.

Measurements of the ionization potentials were made with the following conditions;

i) Electron currents trapped at D 5 μA,
ii) Electron accelerating voltage 0∼+20 V.,
iii) Trap potential at D+100 V.,
iv) Potential at the pusher electrode 0∼+1 V.,

The slits employed in the ion lenses are wider than usual, the slit in ionization chamber 4×10 mm., and the final slit 0.25×10 mm.

Accuracy of the Experimental Results

Two methods have been frequently employed in determining the ionization potentials[5]: (1) the method of linear extrapolation and (2) Honig's[7] critical slope method. Both of them were examined in the present work (see Table I). Values obtained by critical slope method were in better agreement with spectroscopic values. Generally the critical slope method gave reproduceable values. Therefore, this method was employed throughout in the present work.

In Table II representative values of ionization

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[4] H. D. Hagstrum, *Revs. Modern Phys.*, **23**, 185 (1951).

[5] See, for example, G.P. Barnard, "Modern Mass Spectrometry", London (1953).

[6] E.B. Jordan and N.D, Coggeshall, *J. Appl. Phys.*, **13**, 539 (1942).

[7] R.E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

TABLE I
APPEARANCE POTENTIALS MEASURED BY VARIOUS METHODS, eV.

Substance	Linear extrapolation	Critical slope	Spectroscopic
Argon	(15.76)	(15.76)	15.76[a]
Neon	21.68	21.62	21.58[5]
Nitrogen	15.67	15.56	15.58[5]
Hydrogen disulfide	10.62	10.54	10.47[b]

a) Moore's value cited by D.P. Stevenson (*Trans. Faraday Soc.* **49,** 867 (1953)).
b) W.C. Price, *Chem. Rev.*, **41,** 257 (1947).

TABLE II
FIRST IONIZATION POTENTIALS OF MOLECULES, eV.

Substance	Present work (Electron impact)	Values in literature (Electron impact)		Values in literature (Spectroscopic)	
Argon	15.76[a]	15.76[a]	(15.77)[5]	15.76[a]	(15.77)[5]
Neon	21.62±0.05	21.53[b]	(21.61; 21.24; 21.42; 21.57)[5]	21.58[5]	
Hydrogen	15.51±0.10	15.40[c]		15.42[d]	
Nitrogen	15.56±0.10	15.66[b]	(15.60; 15.57)[5]	15.50[e]	
Oxygen	12.45±0.10	12.50[b]	(12.20; 12.39)[5]	12.26[5]	
Methyl alcohol	10.97±0.05	10.95[b]		10.80[f]	
Ethyl alcohol	10.65±0.05	10.60[b]		10.70[f]	
Methyl amine	9.41±0.02	9.41[b]		9.80[f]	
Benzene	9.52±0.10	9.52[b]		9.24[f]	
Toluene	9.20±0.05	9.23[b]		8.82[f]	
Pyridine	9.76±0.05	9.8[h]			
Furan	9.00±0.10	9.05[b]		9.01[g]	

a) Moore, loc. cit.
b) J.D. Morrison and A.J.C. Nicholson, *J. Chem. Phys.*, **20,** 1021 (1952).
c) W. Bleakney, *Phys. Rev.*, **35,** 1180 (1930).
d) H. Beutler und H.-O. Jünger, *Z. Physik.*, **100,** 80 (1936).
e) R.E. Worley and F.A. Jenkins, *Phys. Rev.*, **54,** 305 (1938).
f) W.C. Price, *Chem. Rev.*, **41,** 257 (1947).
g) W.C. Price and A.D. Walsh, *Proc. Roy. Soc.* (London), **A179,** 210 (1941).
h) A. Hastrulid, P. Kusch and J.T. Tate, *Phys. Rev.*, **54,** 1037 (1938).

potentials determined in the present studies are compared with those of previous workers. They include five inorganic gases and seven organic vapours. Observed potentials lie in the range between 9 and 22 eV. In all these examples there is general agreement with the values of the previous workers obtained by electron impact method.

On the comparison with spectroscopic values there exists some divergence in values. But there is no need of perfect agreement among the values of the two methods[8], if the impact value of argon is taken from its spectroscopic value.

In conclusion, it may be said that the use of a single standard gas is justfied and also that ionization potentials of molecules are satisfactorily obtained by the apparatus of this experiment for the samples treated so far.

Summary

Instrumental details of electron impact method for determining ionization potentials are recorded. Further, it is shown that the potential values obtained by the present method are in good agreement with the data reported by the previous workers.

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[8] J.D. Morrison and A.J.C. Nicholson, *J. Chem. Phys.*, 20, 1021 (1952).