Ionization Potentials of Some Organic Molecules. III. Aromatic and Conjugated Compounds

By Hiroaki BABA, Itiro OMURA and Keniti HIGASI

(Received February 7, 1956)

Introduction

There are available considerable numbers of reports dealing with the characteristic properties of aromatic and conjugated molecules. Resonance energy, bond length, dipole moment, absorption spectrum and directive power in substitution reactions have been extensively investigated. But unfortunately little information exists in the literature about the ionization potentials.

In the present article some results of the measurement on the appearance potentials of conjugated molecules will be reported. And an interpretation of the results will be given with special reference to its relation to the ultraviolet data of the same compounds.

Experimental Materials

The samples with a few exceptions were obtained from Kanto Chem. Co., Inc. and purified by distillation whenever possible. The refractive index was measured by D-line at 20°C if not recorded.

Benzene b. p. 80°C, $n^{25}=1.4974$; toluene b. p. 109.2°C; thiophenol $n^{23.5}=1.5882$; aniline b. p. 182.8°C, $n=1.5867$; *o*-xylene b. p. 143°C, $n^{21.6}=1.5031$; *m*-xylene b. p. 138°C, $n^{15.7}=1.4994$; *p*-xylene b. p. 137°C, $n^{16}=1.4970$; pyridine b. p. 115.9°C, $n^{21}=1.5087$; α-picoline b. p. 128–9°C, $n^{16.7}=1.5023$; β-picoline b. p. 142.8–143.0°C, $n^{24}=1.5038$; γ-picoline b. p. 144–144.5°C, $n^{17}=1.5057$; pyrrole b. p. 130.7°C, $n=1.5098$; furan b. p. 32.5°C, $n=1.4212$ and thiophene b. p. 83.8°C, $n^{19.7}=1.5267$.

The samples of phenol, anisole and mesitylene were kindly provided by Dr. S. Nagakura of Tokyo University in the pure form. For the pure sample of cyclo-octatetraene we are indebted to Dr. I. Tanaka, Tokyo Institute of Technology.

TABLE I

FIRST IONIZATION POTENTIALS, eV.

Substance	Present work	Previous workers	
Benzene	9.52±0.10	9.52[a]	(9.24)[b]
Toluene	9.20±0.05	9.23[a]	(8.82)[c]
Phenol	9.01±0.05	9.03[a]	
Thiophenol	8.56±0.02		
Aniline	8.23±0.02		
Anisole	8.56±0.05		
o-Xylene	8.96±0.02	8.97[d]	(8.58)[c]
m-Xylene	9.01±0.02	9.02[d]	(8.58)[c]
p-Xylene	8.86±0.02	8.88[d]	(8.48)[c]
Mesitylene	8.76±0.05	8.79[d]	
Pyridine	9.76±0.05	9.80[e]	
α-Picoline	9.66±0.05		
β-Picoline	9.71±0.05		
γ-Picoline	9.56±0.05		
Pyrrole	8.97±0.05		(8.90)[f]
Furan	9.00±0.10	9.05[g]	(9.01)[f]
Thiophene	9.10±0.20		(8.91)[f]
Cyclo-octatetraene	8.63±0.15		

Values in parentheses refer to spectroscopic potentials.

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

b) W.C. Price and R.W. Wood, *J. Chem. Phys.*, **3**, 439 (1935); W.C. Price, *Chem. Rev.*, **41**, 257 (1947).

c) V.J. Hammond, W.C. Price, J.P. Teegan and A.D. Walsh, *Discuss. Faraday Soc.*, **9**, 53 (1940).

d) F.H. Field and J.L. Franklin, *J. Chem. Phys.* **22**, 1895 (1954).

e) A. Hustrulid, P. Kusch and J.T. Tate, *Phys. Rev.* **54**, 1037 (1938).

f) W.C. Price and A.D. Walsh, *Proc. Roc. Soc.* (London), **A179**, 201 (1941).

g) J.D. Morrison, *J. Chem. Phys.*, **19**, 1395 1951).

Experimental Method and Results

The measurement of the appearance potential was made by an apparatus described in a previous report[1]. The evaluation of the ionization potentials was made by Honig's critical slope method. Argon was employed as the reference standard.

The results of this experiment are recorded in Table I. Agreement with the data by previous workers is seen to be satisfactory.

Discussion

With the progress in the molecular orbital theory, various calculations of electronic properties have been made for a wide range of molecules. It appears not possible, however, for accurate prediction to be made as to the exact values of ionization potentials when dealing with such complicated molecules as are treated in the present work. In the following, only qualitative discussion will be undertaken in regard to some experimental results of this work.

As mentioned in the previous paper[2], the first ionization potential is related to the most loosely bound electron, which, in the majority of conjugated molecules, will be an electron belonging to the highest occupied π-orbital. However, in a heterocyclic molecule containing a nitrogen atom, which has a pair of non-bonding electrons, the ionizing electron may possibly be due to one of the non-bonding electrons. This point is important when discussing the potentials of pyridine and picolines.

Substituted Benzenes.—The effect of substitution on the absorption spectrum of benzene has been investigated by Sklar[3], Herzfeld[4], Nagakura and Baba[5] from the viewpoint of electron migration; and the red shift of the near ultraviolet absorption, caused by an ortho-para directing substituent, has been interpreted as due to the following facts. (1) The migration of electrons from the substituent into the unoccupied ring π-orbitals gives rise to an extra stabilization energy. (2) This extra stabilization energy is greater in the excited state than in the ground state. Later, it was shown by Matsen[6] that the electron migration theory is equivalent to the usual perturbation treatment.

The method of electron migration may be used to explain the ionization potentials of substituted benzenes. When one π-electron belonging to the aromatic ring is ionized, a substituent electron will be allowed to migrate into the previously filled π-orbital. As a result of this migration, the extra stabilization energy of the molecular ion will become great compared with that of the neutral molecule. Then the energy difference between the ionized and neutral states will be less for the substituted molecule than for the unsubstituted one. Thus we can expect that the ionization potential will decrease by the introduction of a substituent into the benzene ring. Actually, the potentials of all the substituted benzenes listed in Table I are lower than that of benzene.

The degree of electron migration, hence, the amount of the extra stabilization energy is dependent on the sort of substituent. It is largely determined by ionization energy of the substituent X: the smaller the ionization energy, the greater is the stabilization energy. However, it depends also upon the magnitude of overlapping between X and the neighbouring carbon atom in the ring. Thus, as Robertson and Matsen[7] concluded from ultraviolet absorption data, the stabilization energy will increase in the sequence

$$CH_3 < OH < SH < NH_2;$$

while the ionization energies of the groups X, estimated from those for HX or CH_3X molecules, are in the order $CH_3 > OH > NH_2 > SH$[6]. We may then expect that the ionization potentials of the substituted benzenes will be in the order

benzene > toluene > phenol > thiophenol
> aniline.

This expectation is fulfilled by our experimental results shown in Table I.

Next, we shall turn to the ionization potentials of polymethyl benzenes. Herzfeld[4] showed for polysubstituted benzenes that the red shift of absorption spectrum is nearly additive. In fact, it is seen from Table II that this rule of additivity holds for polymethyl benzenes. Taking into account the electron migration theory, a similar additivity rule may be expected for the change in ionization potential with methyl substitution. The ionizatioh potential data given in Table II and also the plot of potential values versus the number of methyl substituents in Fig. 1 are all in fair accord with the above view.

---

[1] I. Omura, K. Higasi and H. Baba, This Bulletin, 29, 501 (1956).

[2] I. Omura, K. Higasi and H. Baba, This Bulletin, 29, 504 (1956).

[3] A.L. Sklar, *J. Chem. Phys.*, 7, 984 (1939); *Revs. Modern Phys.*, 14, 232 (1942).

[4] K.F. Herzfeld, *Chem Rev.*, 41, 233 (1947).

[5] H. Baba and S. Nagakura, *J. Chem. Soc. Japan*, 72, 72 (1951); S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, 74, 5693 (1952).

[6] F.A. Matsen, *J. Am. Chem. Soc.*, 72, 5243 (1950).

[7] W.W. Robertson and F.A. Matsen, *J. Am. Chem. Soc.*, 72, 5248 (1950).

TABLE II
ULTRAVIOLET ABSORPTIONS[a)] and IONIZATION POTENTIALS OF POLYMETHYL BENZENES

Substance	ν(0–0)[b)] (cm^{-1})	$\Delta\nu$ (cm^{-1})	I[c)] (eV.)	ΔI (eV.)	
Benzene	38089		9.52		
Toluene	37484	−605	9.20	−0.32	
o-Xylene			8.96	−0.56	Average −0.58
m-Xylene			9.01	−0.51	
p-Xylene			8.86	−0.66	
Mesitylene	36488	−1601	8.76	−0.76	

a) The data on the ultraviolet absorptions were taken from Table III (in ref. 4).
b) ν(0–0) represents the wave-number of the 0–0 transition in the vapor state.
c) I represents the first ionization potential.

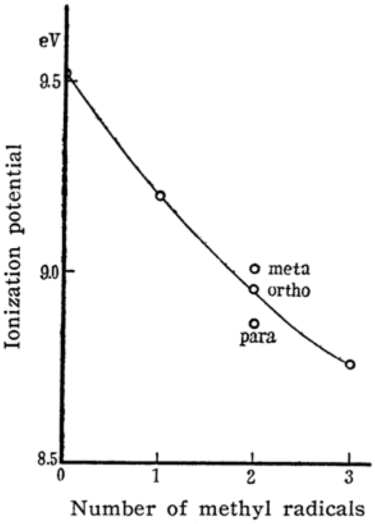

Fig. 1. Variation of ionization potential with the number of methyl radicals in polymethyl benzenes.

Pyridine and Picolines.—According to Table I, the differences of the potential values between pyridine and three isomeric monomethyl pyridines, viz., α-, β-, γ-picolines, are −0.10 eV., −0.05 eV., −0.20 eV., respectively. That is, the lowering of ionization potential caused by the methyl substitution is seen to be less pronounced in pyridine than in benzene (cf. Table II). On the contrary, the red shift of the $\pi\rightarrow\pi^*$ transitions in picolines appears to be not very different from that in toluene[8,9)], so that the perturbation effect of methyl radical on the ring π-orbitals will be almost the same for pyridine and benzene rings. Therefore, if the ionizing electron in question were the one belonging to the π-orbital, the lowering in the ionization potential would not be so small as observed in this experiment. Consequently, it seems very likely that the first ionization potentials of pyridine and its methyl derivatives are primarily determined by the nonbonding $sp^2\sigma$-electron of the N atom.

Indeed, the above view seems to have support from the studies of ultraviolet absorption spectra[8,9,10,11)]. Both in pyridine and picolines, there appear two absorptions of markedly different intensities. The weaker one has been assigned to the transition from the non-bonding orbital of the N atom to the lowest vacant π-orbital ($n\rightarrow\pi^*$ transition), and the stronger one to the transition from the highest occupied π-orbital to the lowest vacant π-orbital ($\pi\rightarrow\pi^*$ transition). The $n\rightarrow\pi^*$ transitions of all these substance occur at the longer wave-lengths, indicating that there is a non-bonding level of the N atom situated above the highest occupied π-level. Therefore, one electron in this non-bonding orbital must be inferred to be responsible for the first ionization*.

Lastly, we shall try to explain the slight decrease in ionization potential upon the methyl substitution. As a result of the resonance among various structures including those of Fig. 2 the methyl group in toluene sends partial negative charge to the carbon atoms of the ortho and para positions. The situation in isomeric picolines may be deduced from this. That is, extra negative charges will appear at the N atoms of α- and γ-picolines, but not at the N atom of β-picoline. Therefore the ionization potentials of the former two substances will become smaller on account of the increased electron density at the N atom, while the potential of β-picoline will remain almost the same as pyridine (cf. Table I).

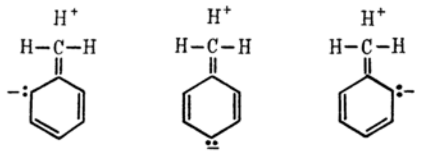

Fig. 2.

Summary

First ionization potentials of 18 aromatic and conjugated compounds were measured by the electron impact method. Seven out of

---

8) J.H. Rush and H. Sponer, *J. Chem. Phys.*, 20, 1847 (1952).
9) H.P. Stephenson, *J. Chem. Phys.*, 22, 1077 (1954).
10) M. Kasha, *Discuss. Faraday Soc.*, 9, 14 (1950).
11) F. Halverson and R.C. Hirt, *J. Chem. Phys.*, 19, 711 (1951).
* There is still some uncertainty about the above assignment. Next, we are intending to measure the ionization potentials of the isomers of diazines and triazines. And then we shall be able fo present more complete and fuller discussion on this problem.

these were newly determined in the present work. Discussion of the results was given with special reference to their relation to the ultraviolet data.

It was suggested that the ionization potentials in benzene derivatives are primarily determined by π-electrons, while those in pyridine and picolines are largely by one of the non-bonding electrons belonging to the N atom in the ring.

The authors with to express their gratitude to Dr. S. Nagakura for valuable criticisms and suggestions, and also to the Ministry of Education for a Grant in Aid.

Research Institute of Applied Electricity
Hokkaido University, Sapporo