# *Ionization Potentials of Some Organic Molecules. II. Aliphatic Compounds*

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## Introduction

There are numbers of molecules the ionization potentials of which are largely determined by non-bonding electrons. When dealing with these molecules it was often assumed that there is some relation between the dipole moment and the ionization potential[1]. First, in the present article, the appearance potentials obtained for seven aliphatic alcohols and three aliphatic amines will be reported. Contrary to the majority of the homologous series the polarity of homologous alcohols remains constant or even decreases with the increase in the carbon number[2,3].

Second, the appearance potentials of two unsaturated aldehydes and two ketones will be treated. From the studies on the dipole moment[4] it is known that there are two factors which affect the electron migration in these molecules, viz., hyperconjugation and inductive effect. For instance, it was inferred that the molecule of acrolein facilitates the transmission of charge to the negative oxygen by means of contribution from structures such as

$$^{+}CH_2-CH=CH-O:^{-} \quad H^{+}\ddot{C}H-CH=CH-O:^{-}$$

If the ionization potential of acrolein is determined by the lone pair of electrons on the oxygen atom, the effect of hyperconjugation will appear in the observed values of potentials.

Lastly, discussion will be presented on the ionization potentials of the molecules, $CH_3CO\cdot X$ (X=OH, $NH_2$, H and $CH_3$).

## Experimental Materials

Alcohols (Kanto Chem. Co., Inc.) were distilled and their purity was checked by measuring the refractive index for D-line at room temperature. Methyl alcohol b. p. 64.5°C, $n^{20}=1.3310$; ethyl alcohol b. p. 78°C, $n^{20}=1.3623$; *n*-propyl alcohol b. p. 97°C, $n^{20}=1.3846$; isopropyl alcohol b. p. 82.4°C, $n^{25}=1.3764$; *n*-butyl alcohol b.p. 117.0°C, $n^{20}=1.3962$; isobutyl alcohol b. p. 107.0°C, $n^{15}=1.3975$; *tert*-butyl alcohol b. p. 82.4°C, $n^{25}=1.3847$.

Amines (Kanto Chem. Co., Inc.) were prepared by distilling off their 25% water; and the degree of purity was examined by a mass spectrometer.

The sample of mesityl oxide in the pure form was very kindly provided by Dr. Nagakura of Tokyo University. Crotonaldehyde was kindly provided by Mr. Maekawa; b. p. 95–110°C, $n^{20}=1.4394$. The remaining samples were obtained from Kanto Chem. Co., Inc. Acrolein b. p. 52–53°C, $n^{20}=1.4005$; acetone b. p. 56.2–56.5°C, $n^{20}=1.3592$; acetic acid b. p. 117–118°C, $n^{20}=1.3723$; ethyl mercaptan b. p. 36–37°C, $n^{20}=1.4307$; acetamide m. p. 79.5°C.

## Experimental Method and Result

The measurement of the first appearance potentials was made by the use of an apparatus described in a previous report[5]. Honig's critical slope method was employed throughout, and examples of this application to butyl alcohols are shown in Fig. 1. It is to be noted in this connection that Morrison and Nicholson[3] reported that

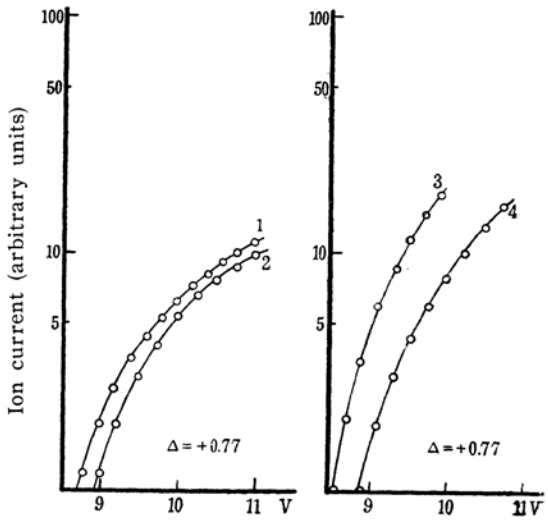


Fig. 1. Relative ionization efficiency curves for alcohols. 1 *tert*-butyl alcohol; 2 isopropyl alcohol; 3 isobutyl alcohol; 4 *n*-butyl alcohol.

1) C.A. Coulson, "Valence", Oxford (1952), p. 186.
2) M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res.* (Tokyo), 26, 242 (1953); 27, 65 (1935).
3) K. Higasi, ibid., 31, 311 (1937).
4) C.P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill Book Co., New York (1955).
5) I. Omura, K. Higasi and H. Baba, This Bulletin, 29, 501 (1956).
6) J. D. Morrison and A. J. C. Nicholson. *J. Chem. Phys.*, 20, 1021 (1952).

no measurement on *n*-butyl alcohol was possible for them on account of the small quantity of molecular ion. Further, Franklin[7] appears to have also failed in measuring the appearance potential of *tert*-butyl alcohol. The reason why such difficulty could be overcome in the present work is probably due to the use of the cylindrical ion lenses[5].

In Table I the results of the present work are collected and compared with the data available. It will be seen that the agreement is satisfactory throughout.

TABLE I

FIRST IONIZATION POTENTIALS, eV.

| Substance | Present work | Previous workers | |
|---|---|---|---|
| Methyl alcohol | 10.97±0.05 | 10.95[5] | (10.80[9]) |
| Ethyl alcohol | 10.65±0.05 | 10.60[5] | (10.70[9]) |
| *n*-Propyl alcohol | 10.42±0.10 | 10.46[5] | (10.70[9]) |
| Isopropyl alcohol | 10.27±0.10 | | |
| *n*-Butyl alcohol | 10.30±0.10 | | |
| Isobutyl alcohol | 10.17±0.10 | | |
| *tert*-Butyl alcohol | 9.92±0.10 | | |
| Methyl amine | 9.41±0.02 | 9.41[5] | (9.80[9]) |
| Dimethyl amine | 9.21±0.05 | | (9.60[9]) |
| Trimethyl amine | 9.02±0.05 | | (9.40[9]) |
| Ethyl mercaptan | 9.21±0.05 | | (9.70[9]) |
| Acetone | 9.89±0.05 | 9.92[5] | |
| Acetic acid | 10.66±0.05 | 10.70[11] | |
| Acetamide | 10.39±0.05 | | |
| Acrolein | 10.25±0.05 | 10.34[5] | |
| Crotonaldehyde | 9.81±0.05 | | |
| Mesityl oxide | 8.89±0.05 | | |

Values in parentheses refer to spectroscopic potentials.

## Discussion

As reported in a previous note[8] the general lowering of the ionization potential with the increase in carbon number is found in the observed values of aliphatic alcohols. When one hydrogen atom is replaced by one methyl radical at $\alpha$ carbon atom, the decrease 0.3–0.4 eV. is found, while such decrease amounts to only 0.2 eV., if the same occurs at $\beta$ carbon atom (see Table II).

Three kinds of explanation can be offered for the observed change of the potential. The first may result from the following assumptions; (1) the ionization potentials of alcohols are solely determined by the non-bonding electrons on the oxygen atom[9]; and (2) alkyl radicals have the property of electron repulsion, the latter being increased along the series[10].

$$-CH_3 < -CH_2(CH_3) < -CH(CH_3)_2 < -C(CH_3)_3.$$

By the so-called inductive effect electrons tend to move from the alkyl group to the oxygen atom, thus reducing the electronegativity of the oxygen atom. Consequently, it would result in the lowering of potentials which is in qualitative agreement with the results shown in Table II.

TABLE II

BRANCH EFFECT OF ALIPHATIC ALCOHOLS ON POTENTIALS (eV.) and MOMENTS (DEBYE)

| Substance | Potential (obs.) | Potential (calcd.) | Moment[3] (gas) | Moment[3] (solution) |
|---|---|---|---|---|
| $CH_3OH$ | 10.97 | [10.95] | 1.69 | 1.62 |
| | (0.32) | | | |
| $CH_2(CH_3)OH$ | 10.65 | 10.54 | 1.69 | 1.66 |
| | (0.38) | | | |
| $CH(CH_3)_2OH$ | 10.27 | 10.07 | 1.63 | 1.66 |
| | (0.35) | | | |
| $C(CH_3)_3OH$ | 9.92 | 9.69 | —— | 1.66 |
| $CH_3CH_2OH$ | 10.65 | 10.54 | 1.69 | 1.66 |
| | (0.23) | | | |
| $CH_2(CH_3)\cdot CH_2OH$ | 10.42 | 10.36 | 1.66 | 1.66 |
| | (0,25) | | | |
| $CH(CH_3)_2\cdot CH_2OH$ | 10.17 | 9.97 | 1.63 | 1.65 |

Potential value in brackets was taken as the standard in calculations.

To argue against the above view, one may point out the fact that the electric moment of alcohols does not increase with the increase in the carbon number[2,4]. But this evidence may not be convincing. There are two dipoles in the molecule: one along the O–H linkage, the other along the C–O linkage and they make an angle with each other. Although the C–O bond moment may increase with the electron transmission toward the oxygen atom, the larger O–H moment will not increase but possibly decrease. Consequently, it is likely that no appreciable increase in the whole moment would result, if such electron displacement actually occurs. One is to note instead that the above series of the electron repelling property have been derived from chemical reactivities and they rest on no sound physical evidence*. If this mechanism of the electron displacement be true, it is highly doubtful whether it is significant enough to produce the observed effect.

The second explanation comes from the application of group orbitals[11]. As is well known this method requires the solution of the secular equation

$$|e_{ij} - E\delta_{ij}| = 0$$

7) J.L. Franklin, Private communications.

8) I. Omura, H. Baba and K. Higasi, This Bulletin, 28, 147 (1955).

9) W.C. Price, *Chem. Rev.*, 41, 257 (1947).

10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell Univ. Press (1951); Table 7-2, p. 71.

* One of the present writers discussed this problem in other place (cf. K. Higasi and K. Hirota, "Theory of Organic Chemistry", Asakura Book Co., Tokyo (1951), Chap. V).

11) J.L. Franklin, *J. Chem. Phys.*, 22, 1304 (1954).

where $i$ and $j$ refer to various groups in the molecule. The roots of secular equation represent the ionization potentials of the molecule, the lowest root being the first ionization potential measured.

Calculation of ionization potentials according to this method has been done by Franklin[11] for methyl, ethyl and *n*-propyl alcohols. In the present work, further calculations are carried out for remaining alcohols, assuming the same values for the constants, $e, b, g,$ and $c$ with those of Franklin. Calculated results are given in the third column of Table II. In view of the fact that this calculation is based on many bold assumptions, it is surprising that the calculated values are in fair accord with those observed.

Both of the views stated above are based on the assumption that the ionization potential is concerned solely with the normal state of neutral molecule before electron impact. Therefore, the third explanation comes from the view that this assumption is not always valid. For instance, Price[9] argues that the effect of alkyl substitution on the ionization potential is due mainly to preferential stabilization of the ionic or excited state. Indeed, his explanation for the ionization potential of RX is in good accord with our results on alcohols. The only regret in regard to this view is that no estimation is possible as to the effect of such a mechanism.

In Table III the measured potentials of

TABLE III

POTENTIALS IN eV. AND MOMENTS IN DEBYE OF ALIPHATIC AMINES

| Substance | Potential (obs.) | Potential[11] (calcd.) | Moment[2,3] (gas) |
|---|---|---|---|
| Methyl amine | 9.41 | [9.41] | 1.28 |
| Dimethyl amine | 9.21 | 8.67 | 1.02 |
| Trimethyl amine | 9.02 | 8.06 | 0.8 |

aliphatic amines are recorded. The calculated values based on group orbital method by Franklin[11] are shown in the same table together with the dipole moment values. It will be seen that both potentials and moments decrease with the increase in the number of methyl groups. Agreement with the calculated values is not good. Possibly, this is a case when the effect of molecular ion stabilization is important.

Before discussing the ionization potentials of unsaturated aldehydes and ketones, attention will be drawn to those of saturated compounds in which the lone-pair electrons of the O-atom play a dominant role in the ionization potential[1] (Table IV). Upon the alkyl substitution the decrease in the potential which is accompanied by the increase

TABLE IV

IONIZATION POTENTIALS (eV.) AND DIPOLE MOMENTS (DEBYE) OF KETONES AND ALDEHYDES

| Substance | Potential (obs.) | Potential (calcd.) | Moment[3] (gas) |
|---|---|---|---|
| HCHO | 10.88[9] | [10.88] | 2.27 |
| $CH_3CHO$ | 10.28[5] | [10.28] | 2.72 |
| $CH_3COCH_3$ | 9.89 | 9.84 | 2.85 |
| $CH_2=CHCHO$ | 10.25 | —— | 3.04 |
| $CH_3\cdot CH=CHCHO$ | 9.81 | 9.74 | 3.67 |
| $(CH_3)_2C=CHCOCH_3$ | 8.89 | 8.75 | 2.84* |

* Moment obtained in solution.

in moment occurs in these molecules. This is in accord with the simple view that the effect of hyperconjugation as well as the inductive effect of the alkyl group cooperate to concentrate the electrons more towards the oxygen atom, thus resulting in a higher CO bond moment and a lower ionization potential.

The situation in acrolein and crotonaldehyde is somewhat complicated, since there are $\pi$-electrons in the C=C bond. The potential decrease on the introduction of one methyl group into the $\beta$ carbon atom of acrolein amounts to 0.44 eV. If this large decrease be attributable to the change in the electron concentration on the oxygen atom*, this would indicate that the electron transfer is greatly facilitated along the $\pi$-bonds. The potential value of mesityl oxide $(CH_3)_2C=C\cdot COCH_3$ is of special interest. It shows a further decrease of 0.92 eV. over the value of crotonaldehyde $CH_3\cdot CH=CHCHO$. For comparison's sake, the results of calculation based on the group orbital method are included in Table IV. The calculated values are in accord with the observed.

Lastly, the potential values of $CH_3CO\cdot X$ will be considered. According to the present measurement (Tables I and IV), $CH_3CO\cdot OH$ 10.66, $CH_3CO\cdot NH_2$ 10.39, $CH_3CHO$ 10.28 and $CH_3CO\cdot CH_3$ 9.89 eV. If the ionization potential is largely determined by the non-bonding electrons at the O-atom, the sequence of $OH>NH_2>H>CH_3$ would indicate that the groups attract electrons more strongly along this series from the oxygen atom. Indeed, this expectation may be fulfilled, if only the inductive mechanism[10] be taken into consideration. But this is a problem which needs further investigation, because there are complicating factors including another mechanism of the electron displacement.

* A support for this view may be found in McMurry's work (*J. Chem. Phys.*, 9, 231, 241 (1941)). According to him, in ketones and aldehydes including acrolein and croton aldehyde, one of the non-bonding electrons corresponds to the most loosely bound electron.

**Summary**

Ionization potentials of seven alcohols, three amines and nine other aliphatic compounds were determined by a mass spectrometer of Hagstrum type. In view of the fact that no reliable explanation of the ionization potentials of molecules has been given an examination of the possible interpretations of the results was presented. The relation of ionization potentials to the dipole moments, non-bonding electrons and the group orbital method are briefly discussed.

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