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Lone Pair Ionization Potentials of Carboxylic Acids Determined by He(I) Photoelectron Spectroscopy

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Photoelectron spectra of some simple carboxylic acids and halogen substituted acetic acids were observed. Each spectrum contains a band which is associated with the ionization from an oxygen lone pair (n_O) orbital of carboxyl group. The band associated with the n_O orbital is clearly separated from other bands, and its shape and width are quite similar among the various carboxylic acids. In the spectra of halogen substituted acetic acids, n_O band appears around the region of the lone pair bands of halogen atoms. The ionization potentials for oxygen lone pair orbital of carboxylic acids are measured and compared with the results of some semi-empirical SCF MO calculations. The agreements are quite satisfactory when ionization potentials are obtained from the difference of total energies of neutral molecule and its corresponding cation calculated using CNDO/2 or INDO method. MINDO/2 method also gives excellent values when Koopmans' theorem is applied.

When a certain functional group of a molecule is expected to play a special role in a chemical reaction, it is desired to know the intrinsic properties of the group. There are many physicochemical techniques being used for that purpose, *e.g.* IR, Raman, UV, NMR, *etc.* If a functional group has electron orbitals which are considered to be essentially localized on the group, the orbital energies should be a measure of the intrinsic properties of the group, too. The orbital energies have usually been determined experimentally as ionization potentials of molecules from vacuum ultraviolet absorption spectrum, electron impact, or photoionization method. Photoelectron spectroscopy, developed by Turner *et al.*,[1)] has recently been recognized to have great potentialities as a tool which measures ionization potentials of various free molecules. It enables us to observe all orbitals of molecules which have less binding energy than the energy of irradiating light, frequently helium resonance line 584 Å (21.22 eV). The shape and/or structure of each band in the high resolution photoelectron spectrum are useful for the assignment of the bands.

Carboxyl group is known to have an oxygen lone pair (n_O) orbital and π orbitals. Theoretical calculations predict that the n_O orbital is composed mainly (50—80 per cent) of carbonyl oxygen atomic orbitals in various carboxylic acids.

It was our interest to study the extent of disappearance of the feature of these particular bands in the photoelectron spectra and the orbital energy variation as carboxylic acid molecule becomes larger. This paper deals with the results of some simple mono carboxylic acids and halogen substituted acetic acids. They are compared with the results of semi-empirical molecular orbital calculations such as CNDO/2,[2)] INDO,[2)] and MINDO/2[3)] method to know how well these calculations can predict the ionization potentials of various carboxylic acids.

Experimental

The details of the photoelectron spectrometer used have already been reported.[4)] The exciting light was He(I) resonance line which was produced by DC discharge through a glass capillary with a hollow cathode. The electron energy analyser was of an electrostatic type with parallel plates coated with benzene soot. With this spectrometer the peak width of Xe $^2P_{3/2}$ was 27.5 meV. Although the most of the sample gases were measured at this resolution, we had to decrease the resolution to about 50 meV for measuring monoiodo acetic acid, since its vapor pressure was small.

All samples were of G.R. grade and used without any further purification. Variations of appearance potentials of photoelectron peaks for carboxylic acids during measurements were so large that preliminary mixing of reference gas, xenon, into the sample gas was essentially needed to measure the ionization potentials accurately. Usually the spectra were measured after more than 30 min running of sample gas, since shift of the kinetic energy of photoelectron to lower energy side with the elapse of time was always noticed.

Results and Discussion

In Fig. 1, the photoelectron spectrum of formic acid is shown. At least five bands are distinguishable and three of them have clear vibrational structures. The spectrum appears quite similar to the spectrum reported by Turner and co-workers.[1,5)] However the structures of the second band are somewhat different from their results. Measurements for DCOOD, DCO-OH, and HCOOD have also been performed and their vibrational structures have been studied. The details of the results will be reported elsewhere.[6)]

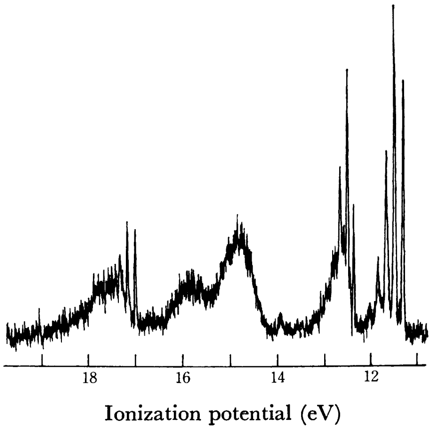

Fig. 1. Photoelectron spectrum of formic acid.

In Figs. 2—5, the spectra of a series of aliphatic carboxylic acids are shown. The larger the alkyl group, the less clear the vibrational structures, and the closer the bands overlap. However it is observed that the first band is always separated from the second, that its shape and width are much the same, and that there always appears a band at a potential of 16—18 eV.

The spectra of trifluoro-, monochloro-, monobromo-,

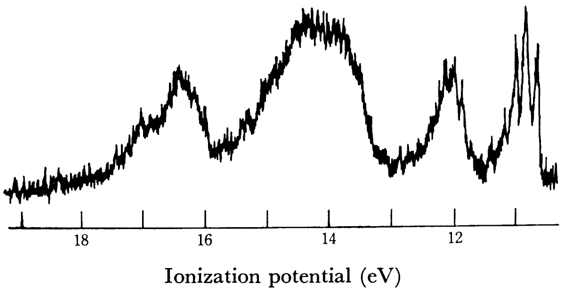

Fig. 2. Photoelectron spectrum of acetic acid.

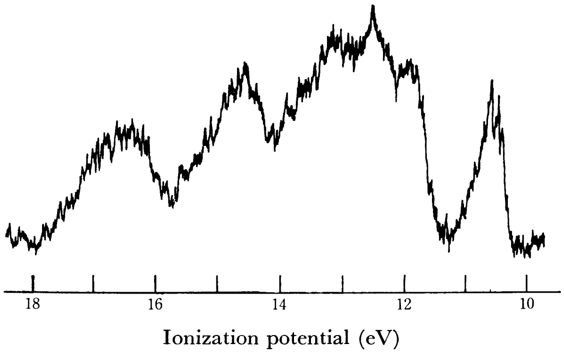

Fig. 3. Photoelectron spectrum of propionic acid.

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1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York (1970).

2) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York (1970).

3) N. Boder, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).

4) Y. Yokoyama, I. Watanabe, and S. Ikeda, *Bunseki Kagaku*, **20**, 1502 (1971).

5) C. R. Brundle, D. W. Turner, M. B. Robin, and H. Basch, *Chem. Phys. Lett.*, **3**, 292 (1969).

6) I. Watanabe, Y. Yokoyama, and S. Ikeda, *ibid.*, **19**, 406 (1973).

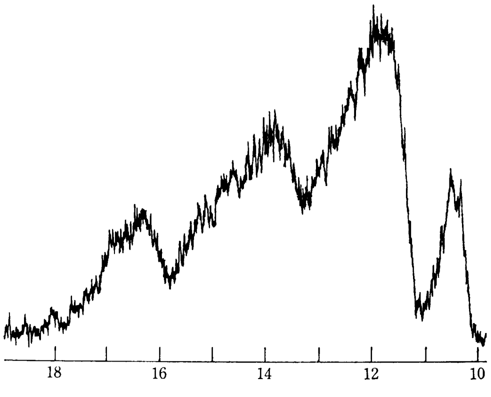

Fig. 4. Photoelectron spectrum of *n*-butyric acid.

and monoiodo-acetic acids are shown in Figs. 6, 7, 8, and 9, respectively. Although the intensity of the peaks of trifluoroacetic acid is relatively weak and the spectrum has a lot of noise, six bands are clearly separated. In this spectrum no vibrational structure is distinguishable. The first and the second bands are a little broader than those of acetic acid and, however, the band shapes and the separation of these bands are almost identical. The molecular orbital calculations indicate these bands are associated with the ionizations from n_O and antisymmetric π (π_2) orbital of carboxyl group.

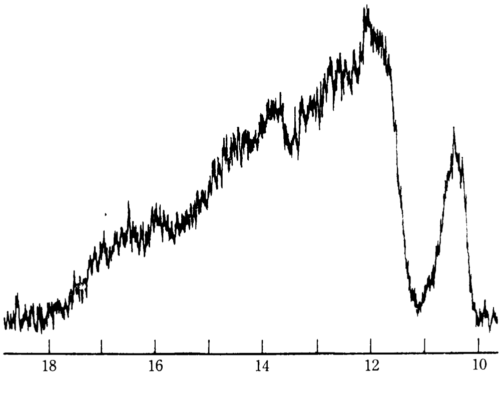

Fig. 5. Photoelectron spectrum of *iso*-butyric acid.

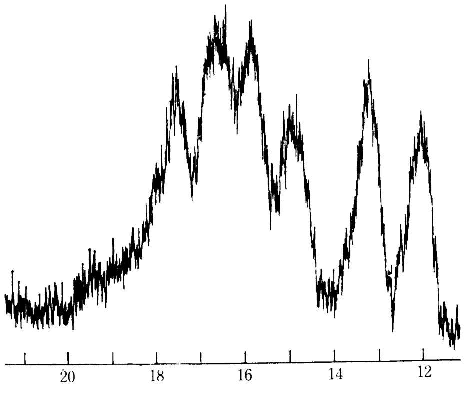

Fig. 6. Photoelectron spectrum of trifluoroacetic acid.

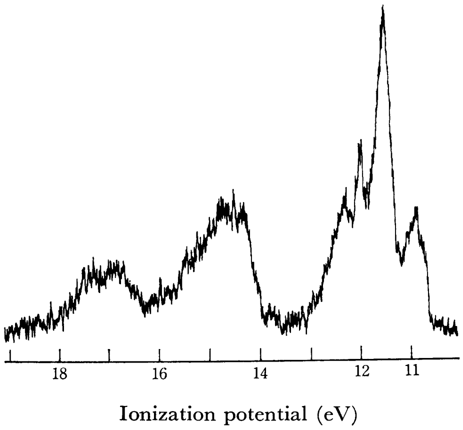

Fig. 7. Photoelectron spectrum of monochloroacetic acid.

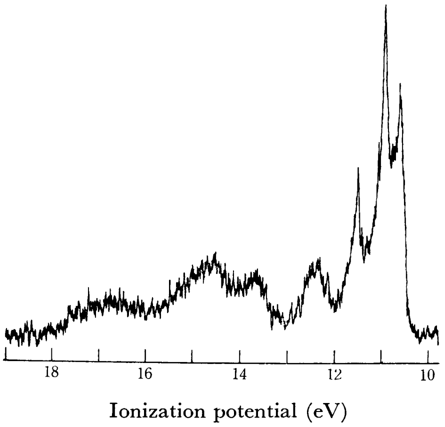

Fig. 8. Photoelectron spectrum of monobromoacetic acid.

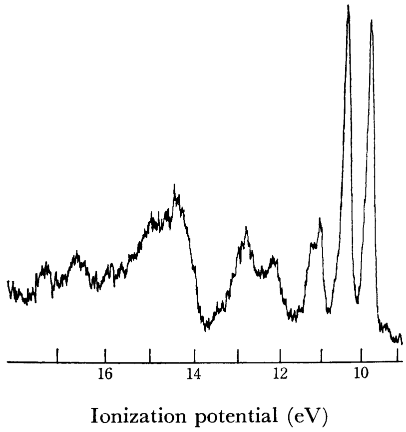

Fig. 9. Photoelectron spectrum of monoiodoacetic acid.

The spectra of the other three halogen substituted acetic acids are more complex, since around the bands from the orbitals localized mainly on the carboxyl group appear halogen lone pair bands which split into two components by the effect of the spin-orbit interaction. The spin-orbit splittings for many molecules containing halogen atoms have been reported to be about 80 meV for chlorine, 0.3 eV for bromine, and 0.6 eV for iodine.1,7) With the aid of these values the

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7) a) A. B. Cornford, D. C. Frost, C. A. McDowell, J. L. Ragle, and I. A. Stenhouse, *J. Chem. Phys.*, **54**, 2651 (1971); *b*) J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *ibid.*, **53**, 178 (1970).

Table 1. Ionization potentials for oxygen lone pair orbitals (eV)

	CNDO/2		INDO		MINDO/2	P. I.	Present work	
	a)	b)	a)	b)	a)	c)	Vertical	Adiabatic
HCOOH	14.69	12.11	13.70	11.38	11.44	11.05	11.52	11.33
CH_3COOH	13.87	11.22	12.96	10.61	10.95	10.37	10.84	10.65
C_2H_5COOH	13.46	11.01	12.65	10.42	10.65	10.24	10.72	10.54
$CH_3(CH_2)_2COOH$	13.33	10.89	12.51	10.31	10.46	10.16	10.64	10.46
$(CH_3)_2CHCOOH$	13.28	10.87	12.55	10.32	10.57	10.02	10.50	10.33
$CH_3(CH_2)_3COOH$	13.21	10.84	12.42	10.26	10.29		10.5(3)	
$(CH_3)_2CHCH_2COOH$	13.18	10.74	12.43	10.20	10.45		10.5(1)	
CF_3COOH	14.56	12.82	13.87	12.26			12.00	
$ClCH_2COOH$	13.75	11.55					10.99	
$BrCH_2COOH$							11.0	
ICH_2COOH							11.03	

a) Obtained by the use of Koopmans' theorem.
b) The difference between the total energies of molecule and its corresponding cation.
c) The results of photoionization method. Ref. 8.
Ionization potentials of carboxylic acids determined by others are, formic (adia. 11.33,[d] 11.35,[e] vert. 11.51,[d] 11.52[e]), acetic (adia. 10.70,[d] 10.69,[e] vert. 10.87,[d] 10.86,[e]), propionic (adia. 10.44,[e] vert. 10.70[e]), isobutyric (adia. 10.33,[e] vert. 10.50[e]), trifluoroacetic (vert. 12.0[e]).
d) Ref. 13.
e) Ref. 14.

spectra are interpreted.

The first band in the spectrum of monochloro acetic acid is originated from n_O orbital of carboxyl oxygen and the next sharp peak from chlorine lone pair orbital. The spin-orbit splitting for chlorine atom is not observed because of the broadness of the peak. The order of halogen lone pair orbital and n_O orbital of carboxyl group is reversed in the case of monoiodoacetic acid. In the spectrum of monobromoacetic acid, the first two bands are originated from bromine lone pair orbital and the n_O band is considered to coincide with the second peak of the bromine lone pair bands.

Comparison of the Results Obtained by Photoelectron Spectroscopy and Photoionization Method. In Table 1, ionization potentials for various mono carboxylic acids determined by the photoelectron spectroscopy and photoionization method[8] are listed. The photoionization method always gives smaller adiabatic ionization potentials by 0.28—0.31 eV than the photoelectron spectroscopy does. The differences are quite the same. The first band of all of these molecules originates from oxygen lone pair orbital and photoelectron spectra show that the bands so much resemble each other in both shape and band width, and that the first band is clearly separated from the second. Since the photoionization method is particularly sensitive to the structure around the onset potential for the highest occupied orbital, these special conditions should be the main reason for the differences of the ionization potentials obtained by the photoionization method from our results to be constant.

Ionization Potentials Predicted from MO Calculations. In many cases, ionization potentials have been estimated by applying Koopmans' theorem to the results of molecular orbital energy calculation. When semi-empirical SCF MO calculations, such as CNDO or INDO, are performed, it is well known that each eigen value after multiplication by about 0.8[9] or subtraction of about 4 eV[10] approximately agrees with ionization potential experimentally measured. It is also known that the correlation between the eigen values calculated by MINDO/2 method and ionization potentials is quite satisfactory.[3]

We have performed CNDO/2, INDO, and MINDO/2 calculations. Ionization potentials have been estimated by the use of Koopmans' theorem. In addition, ionization potentials have been obtained from the difference between the total energy of the neutral molecule, E^0, and that of the corresponding cation radical in the same geometry, E^+, calculated by the unrestricted CNDO/2 and INDO method. The values obtained are listed in Table 1 and should be compared with the vertical ionization potentials observed.

The orbital energies by CNDO/2 and INDO method are steadily larger than the observed ionization potentials, and the agreement of the differences, E^+-E^0, with the observed ionization potentials is excellent. On the occasion of application of Koopmans' theorem to calculation by CNDO/2 and INDO methods, the discrepancy of energy in calculated and observed values is derived from errors due to arbitrariness of parameters used in calculation by CNDO/2 and INDO methods as well as both neglect of reorganization energy and assumption of constancy of relativistic and correlation energies.[11] On the other hand, the errors could successfully be cancelled in the difference, E^+-E^0.

Ionization potentials taken as the difference, E^+-E^0,

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[8] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

[9] J. W. Rabalais, *J. Chem. Phys.*, **57**, 960 (1972).

[10] a) D. W. Davies, *Chem. Phys. Lett.*, **2**, 173 (1968); b) D. C. Frost, F. G. Herring, C. A. McDowell, M. R. Mustafa, and J. S. Sandhu, *ibid.*, **2**, 663 (1968); c) G. R. Branton, D. C. Frost, F. G. Herring, C. A. McDowell, and I. A. Stenhouse, *ibid.*, **3**, 581 (1969).

[11] W. G. Richards, *Int. J. Mass Spectr. Ion Phys.*, **2**, 419 (1969).

using CNDO/2 method are larger than the observed ones. The same procedure using INDO method gives smaller values. MINDO/2 method is superior in predicting ionization potentials to the above methods from the view point of simplicity of calculation. Our computer program for INDO method was available only for trifluoroacetic acid and CNDO/2 program for trifluoro- and monochloroacetic acid among the halogenated acids. The difference method using INDO predicts excellent value for trifluoroacetic acid.

All calculations we have performed predicted that the level of n_O orbital is higher than that of π_2 orbital in all carboxylic acids, and that the n_O orbital is the highest occupied orbital in the aliphatic carboxylic acids.

Difference of n_O-π_2 Levels. In RCOX where X is OH, OR′, or NR'_2, it has been reported that the separation between n_O and π_2 orbital varies with R and X groups and that the π_2 orbital is particularly sensitive to changes in the X group and the n_O orbital is sensitive to changes in the R group, since the π_2 orbital has a large population on the X group and the n_O orbital has a greater population on the carbonyl carbon than the π_2 does.[12]

In the present work, as the alkyl group of the carboxylic acid becomes larger, the separation between the first and the second band increases. The gap between the first and the second band in the *iso*-tutyric acid is wider by 0.2 eV than that in the *n*-butyric acid. The electron releasing effect of the alkyl group and the atomic orbital population analysis seem to explain these results. However, such an explanation is not always applicable, since the substitution of all hydrogen atoms in the methyl group in acetic acid with fluorine atoms which have a strong electron withdrawing effect considerably shifts the n_O and π_2 bands to greater energy side but the gap in trifluoroacetic acid is almost the same as in acetic acid.

The molecular orbital calculations have been carried out on a NEAC 2200/N700 computer at Osaka University Computer Center.

Notes Added in Proof

After the completion of this paper came to hand two very important papers dealing with the photoelectron spectra of carboxylic acids.[13,14] Ionization potentials reported in these papers are added in a margin of Table 1. The spectra of dimers and complexes of carboxylic acids have been reported by Thomas.[14] From his calculated dimer-monomer ratios and spectra of dimers, we believe that contribution of dimers in the present work is negligible.

From our expanded spectrum of n_O band of acetic acid, from which we have determined the ionization potentials, it appears that the band has at least three vibrational components and is more complex than the one reported by Sweigart and Turner.[13] This might cause the ionization potentials of acetic acid in the present work to be a little smaller than the values reported by them.

It was recognized that the spectrum of the second band (π_2) of formic acid reported by Turner and co-workers[1] may contain a peak (12.61 eV) from impurity water.[15]

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[12] J. Daintith, R. Dinsdale, J. P. Maier, D. A. Sweigart, and D. W. Turner, "Molecular Spectroscopy 1971, Proc. of the 5th Conf. on Molecular Spectroscopy, Brighton, 1971," Institute of Petroleum, (1972), p. 16.

[13] D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5592 (1972).

[14] R. K. Thomas, *Proc. Roy. Soc. Ser. A*, **331**, 249 (1972).

[15] D. W. Turner, Private communication.