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Mass Spectrometric Study of Photoionization. II. Mass Spectra by the Use of Resonance Lines of Argon and Helium

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An emission line of He II was generated at 304 Å (40.80 eV) from a microwave plasma light source operated in the standing wave mode. On the other hand, the plasma without the standing wave mode emits only the resonance line of He I at 584 Å (21.21 eV). A resonance line of Ar I was emitted at 1048 Å (11.82 eV) by argon carrier gas flowing through a capillary tube. The mass spectra of propane, *n*-butane, propylene, benzene, and isoamyl acetate obtained by the use of the emission line of He II at 304 Å were not very different from those of the electron impact method at 50 eV. The positive-charge distribution on each atom of the ionized molecules is estimated from the total ion yield of the molecule. In the fragmentation processes of isoamyl acetate, the intensity of the fragment ion (CH_3CO^+) including carbonyl group rose rapidly with the increase in the photon energies obtained by the resonance lines of Ar I, He I, and He II. At these photon energies, the ratios of the fragment ion, CH_3CO^+, to that of $C_5H_{10}^+$ were 0.17, 0.43 and 2.0 respectively.

The processes of photoionization are investigated by using a mass spectrometer with a vacuum monochromator or a resonance-discharge light source. Inghram(1) and Dibeler(2) reported results obtained using the former technique. A mass analysis of ions produced by the resonance line was first reported by Lossing and Tanaka.(3) Brion(4) observed the difference in mass spectra appearing between the electron impact and the photon impact using the resonance line. Inghram(1) and Tanaka(3) used a light source with a lithium fluoride window, but Dibeler(5) and Brion(4) described some preliminary experiments on the performance and characteristics of a windowless light source. Koyano, Omura and Tanaka(6) reported on the dimeric ions of acetylene, $C_4H_3^+$ and $C_4H_2^+$, which were produced by the chemi-ionization reaction between excited- and ground-states of acetylene when acetylene was irradiated with Lyman alpha (1216 Å).

In spite of these successes in this field, the maximum energy of a photon has been limited to the helium resonance line at 584 Å, whose energy corresponds to 21.21 eV. The results of the analysis of organic compounds obtained by the resonance line of He I at 584 Å can not be compared directly with those of the electron impact method, since we have only the data on an electron impact of 50 or 70 eV. Therefore, in order to apply the photon-impact data to the analysis of organic compounds the photon energy should come up to the resonance line of a higher energy, about 50 eV. Omura and Doi(7) have developed a new microwave-discharge light source emitting the emission line of He II at 304 Å, the energy of the line corresponds to 40.80 eV.

The purpose of the present paper is not to describe the principles of the operation of the discharge light source, but to discuss the mass spectra of several organic compounds ionized by the resonance lines of Ar I at 1048 Å, or of He I at 584 Å, or the emission line of He II at 304 Å. For isoamyl acetate, the positive charge migration will be discussed, in terms of the ratio of principal fragment ions.

Experimental

Measurements. The apparatus employed in this paper is a Hitachi RMU-6D-type mass spectrometer. The main part of the light source consists of a quartz discharge tube, a metal shutter plate with a pin hole (1 mmϕ), and a small chamber for differential pumping (see Fig. 1). A needle valve is provided to control the flow rate of carrier gas (helium or argon) into the quartz capillary discharge tube. The microwave power supply, 2.45 GHz and 50 W power, is used for the excitation of the carrier gas. Typical operating conditions are: helium pressure in the quartz discharge tube, 1—5 mmHg; microwave output 50 W; quartz tube with an inner diameter of 8 mm and a length of

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1) B. Seiner, C. F. Giese and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

2) V. H. Dibeler and R. M. Reese, *ibid.*, **40**, 2034 (1964); **40**, 2046 (1965); **42**, 1842, 3791 (1965).

3) F. P. Lossing and I. Tanaka, *ibid.*, **25**, 1031 (1956).

4) C. E. Brion, *Anal. Chem.*, **37**, 1706 (1965).

5) V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Std.*, **68**, 409 (1964).

6) I. Koyano, I. Omura and I. Tanaka, *J. Chem. Phys.*, **40**, 2734 (1964); **44**, 3850 (1966).

7) I. Omura and H. Doi, *Japan J. Appl. Phys.*, **6**, 275 (1967).

300 mm. Photon beams ejected from the microwave discharge light source pass through a capillary tube provided to take care of the pressure difference and enter the ionization chamber. In the case of a new light source, the photon energy is determined by means of the resonance line of the carrier gas (He or Ar) flowing through the quartz tube; that photon energy which is higher than the resonance line of the helium is generated by using the following techniques.

For the helium light source, when the metal shutter plate is placed in front of the quartz discharge tube, the emission line of He II at 304 Å is generated by the standing wave produced in the plasma. On the other hand, when the shutter plate is removed, the plasma light source emits only the resonance line of He at 584 Å. In the case of the argon light source, the argon plasma light source used in the former method generated emission lines of various wavelengths, corresponding to the multiple-charged argon atom. Therefore, this light source can not be employed as a monochromatic argon lamp. On the other hand, the light source operated in the latter method emits the resonance lines or Ar I at 1048 Å, and 1067 Å. These vacuum ultraviolet lines are observed by the use of a 0.5-m Seya-Namioka monochromator containing a tripartite, concave grating blazed for 700 Å, they were identified by the aid of the reports of Robinson[8] and Edlen.[9]

Photon beams passing through the capillary tube provided for the differential pumping and the ionization chamber impinge on the surface of the photocathode (Au). The secondary electrons from the photocathode are measured by the collector plate (Pt), biased +22.5 eV with respect to the photocathode (Au). The ion source housing is evacuated differentially by two pumps, as is shown in Fig. 1. The pressure difference between the light source and the ionization chamber housing is of the order of 10^4, while the pressure difference between the ionization chamber and the analyzer tube is of the order of 10^3. Ion currents are measured with an electron multiplier with a total gain of 10^7 after mass analysis.

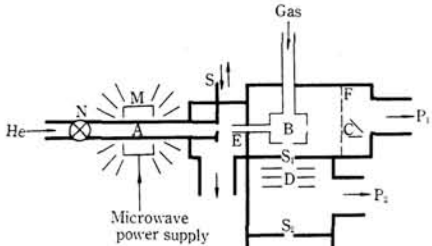

Fig. 1. Schematic diagram of photon and ion sources. A, microwave light source, quartz tube I. D. 8 mm, pressure 1—5 mmHg; B, ion chamber; C, photon collector; D, ion focusing lens; E, capillary tube I. D. 0.5 mm, length 40 mm; F, collector shield mesh, earth potential; M, microwave resonant cavity, supplying power 50 W, 2.45 GHz; N, needle valve; S, metal shutter plate; S_1, differential pumping orifice 1 mmϕ; S_2, differential pumping orifice 0.1 mmϕ; P_1, mechanical pump 350 l/min; P_2, oil diffusion pump 400 l/s; P_3, oil diffusion pump 120 l/s.

Results and Discussion

Mass Spectra. The mass spectra of organic compounds have been reported on extensively with an ionizing electron of higher than 50 eV, but the data of the lower-energy electron impact method have not yet been arranged into a volume. The mass spectra obtained in the low-energy electron-impact method, in general, can not be directly compared with the high-energy data, especially in the case of organic compounds.[10-12] In the case of the photon impact, the mass spectra obtained with low energy and with high energy may never coincide with each other. For the comparison of the mass spectra obtained with the electron or the photon of the same energy, there are problems of the ionization cross section or thermal decompositions of the molecule.[4] Therefore, it is estimated that the two spectra are not in good agreement with each other.

The mass spectra observed using the resonance lines of Ar I at 1048 Å (11.82 eV), He I at 584 Å (21.21 eV), and He II at 304 Å (40.80 eV) are first given for propylene and isoamyl acetate in

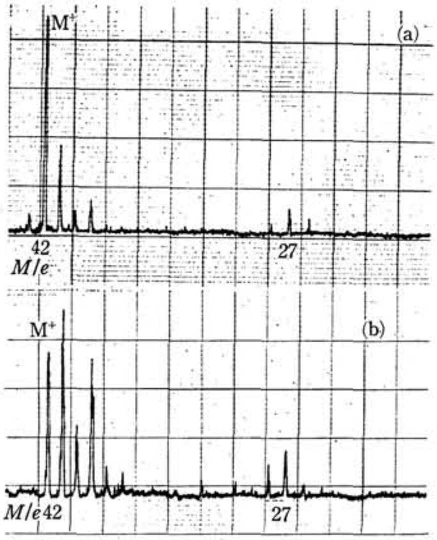

Fig. 2. Mass spectra of propylene obtained with photoionization.

a) Resonance line of He I at 584 Å=21.21 eV

b) Emission line of He II at 304 Å=40.80 eV

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8) J. C. Boyce and H. A. Robinson, *J. Opt. Soc. Am.*, **26**, 133 (1936).

9) B. Edlen, *Reports Proc. Phys.*, **26**, 181 (1963).

10) L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957).

11) A. B. King and F. A. Long, *ibid.*, **29**, 374 (1958).

12) I. Omura, This Bulletin, **34**, 1227 (1961); **35**, 1845 (1962).

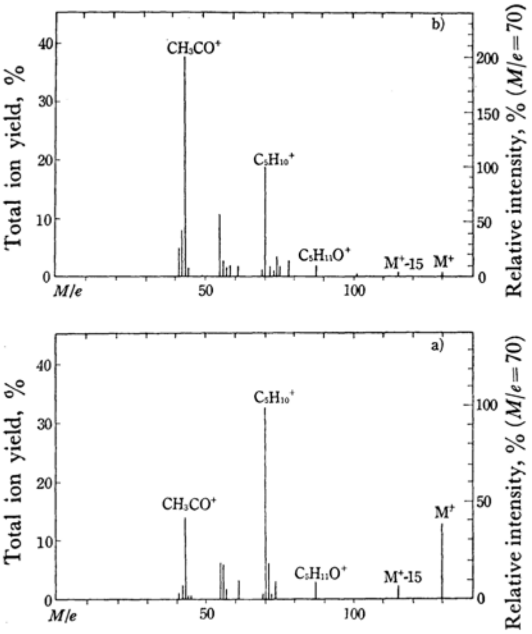

Fig. 3. Mass spectra of isoamyl acetate obtained with photoionization.
a) Resonance line of He I at 584 Å = 21.21 eV
b) Emission line of He II at 304 Å = 40.80 eV

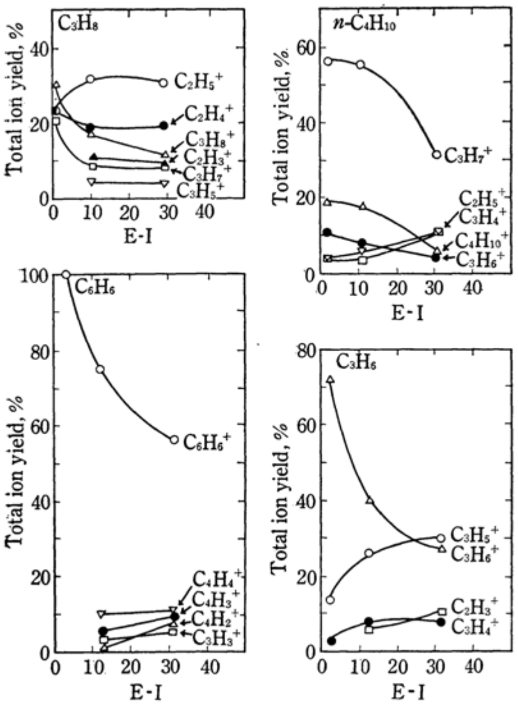

Fig. 4. Variation of total yield of the principal ions occurring from some hydrocarbon molecules with the excess energies.
E, photon energy; low energy Ar I, middle energy He I and high energy He II,
I, ionization potential of molecule.

TABLE 1. RELATIVE INTENSITIES OF SUBSTANCES a) PROPYLENE, b) ISOAMYL ACETATE

a) Propylene

M/e	Photoionization Ar I 1048 Å (11.82 eV)	Photoionization He I 584 Å (21.21 eV)	Photoionization He II 304 Å (40.80 eV)	Electron impact API (50 eV)
26				11
27		15	33	39
39	5	58	67	73
40	5	25	25	29
41	19	92	100	100
42	100	100	90	70
43	6	8	8	2

API: American petroleum institute research project.

b) Isoamyl acetate

M/e	Photoionization Ar I 1048 Å (11.82 eV)	Photoionization He I 584 Å (21.21 eV)	Photoionization He II 304 Å (40.80 eV)	Electron impact API (50 eV)
41	4	4	24	20
42		8	36	24
43	15	43	210	175
44		1	9	5
55	6	19	57	68
56	14	16	14	5
57	4	6	8	6
61	6	10	12	22
69		3	7	10
70	100	100	100	100
71	13	19	11	8
72	3	4	5	2
73	4	9	18	19
87	6	9	15	17
115	6	7	2	1
130	21	39	0.6	0.4

API: American petroleum institute research project.

Fig. 2 and Fig. 3. Table 1 shows the patterns of the two molecules obtained by the photon- and electron-impact methods. The spectra of propylene and of isoamyl acetate irradiated with He I at 584 Å may be compared with the electron-impact data at 20 eV. From the table, it can be said that the patterns of He II at 304 Å are not very different from those of the electron-impact method. The comparison gives useful example for analyzing other data with higher-energy photon-impact spectra.

Total Ion Yield. A positive charge distribution on each atom of an ionized molecule may give a path of decomposition into fragment ions, and the relative intensities of the fragment ions

TABLE 2. RELATION OF IONIZATION BETWEEN SUBSTANCES AND LIGHT SOURCE

Light source	Resonance line Å, eV		Ne 21.58*	Xe 12.16*	CH_4 13.04*	C_3H_6 9.73*
Ar I	1048 (11.82)	1067 (11.62)	×	×	×	○
He I	584 (21.21)		×	○	○	○
Ar II—VII	462 (26.82)	585 (21.21)	○	○	○	○
He II	304 (40.80)	584 (21.21)	○	○	○	○

○ Ionized × Not ionized * Ionization potential, eV

will change with the increase in the excess energy of the ionized molecule. Therefore, the total ion yield obtained as a function of the ionizing energy may give some useful information about the migration of the positive charge within the molecule. The total ion yield changes to a large extent with the excess energy in a region slightly above the ionization potential of the molecule.[11] The ion yield tends to an almost constant value in a higher region of the excess energy. This is claimed by Eyring[13] for rather simple molecules, but it has not yet been reported for larger molecules than the above. In this paper, some results with simple molecules will be given first, and then isoamyl acetate will be taken as a special example to discuss whether or not the statement about the simple molecules is applicable here also,

The total ion yields of propane, *n*-butane, propylene, and benzene as the functions of the excess energy are shown in Fig. 4. The abscissa, *E-I*, is the excess energy of the ionizing photon over the ionization potential of the molecule. The photon energies used are the resonance lines of Ar I at 1048 Å and He I at 584 Å, and the emission line of He II at 304 Å. Therefore, the information suggesting the fragmentation process of the ionized molecule is given for the region of energy lower than the energy of He II at 304 Å. Moreover the true ion yield curve in the low-energy region below about 12 eV can not be obtained from the present experiment.

The total ion yields in the low energy region are classified into four types in the case of the electron-impact method. Type I decreases rapidly with an increase in the ionizing energy; Type II rapidly rises to a maximum at an excess energy of 5—10 eV above an appearance potential and then decreases to a nearly constant value; Type III rises to a nearly constant value without passing through a maximum, and Type IV increases slowly with an increase in the ionizing energy.

The $C_2H_5^+$ ion appears from propane and *n*-butane when those molecules are irradiated with the light source of Ar I at 1048 Å. The appearance potentials of the $C_2H_5^+$ ion from those molecules are 12.24 and 12.55 eV respectively. For propylene, $C_2H_5^+$ and $C_3H_4^+$ ions are detected by the light source of Ar I, but the $C_3H_2^+$ and $C_2H_4^+$ ions can not be detected by this light source. The appearance potentials of $C_3H_5^+$, $C_3H_4^+$, $C_3H_2^+$ and $C_2H_4^+$ ions are 12.11, 12.52, 13.80, and 12.85 eV respectively. These ions ($C_3H_5^+$ and $C_3H_4^+$) may be generated by the photoelectron bombardment emitted by the ionization chamber wall. In the ionization chamber, the intensities of the photoelectrons are approximately of the order of one percent of the photon causing the ionization. The relations between the energies of the light source and the ionization of the substances are shown in Table 2.

The ion yield curve of isoamyl acetate is shown in Fig. 5. The yield curve gives some important information: 1) The molecular ion rises to a maximum at an excess energy of 20 eV, and they decreases rapidly to a very small value; 2) The fragment ion including the carbonyl group (*M*/*e*= 43) rises rapidly with an increase in the excess

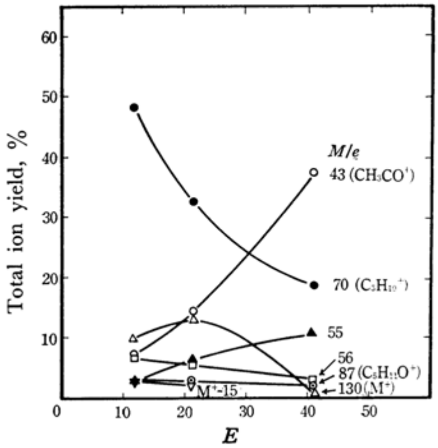

Fig. 5. Variation of total yield of the principal ions occurring from isoamyl acetate with the photon energies.
E, photon energies; low energy Ar I, middle energy He I and high energy He II.

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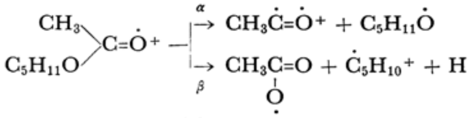
[13] E. M. Eyring and A. L. Wahrhafting, *J. Chem. Phys.*, **34**, 23 (1961).

energy; 3) The fragment ion ($M/e=70$) is very high at a low excess energy, but it decreases rapidly with an increase in the photon energy, and 4) The fragment ion ($M/e=55$) increases slowly with the photon energy.

Figure 5 suggests that the probability of the positive charge distribution on each fragment is changed by the excess energy with relation to the ionized molecule. It is well known that the most facile ionization process corresponds to the removal of the non-bonding electron from the oxygen atom in the case including the carbonyl compound. However, the mass spectra of isoamyl acetate obtained from this experiments suggest that the positive charge in the ionized molecule is distributed more probably on the $C_5H_{10}^+$ group than on the CH_3CO^+ group at a lower excess energy.

In the case of the mass spectra observed by the photon of a high energy, the most intense peak appears at M/e 43 (CH_3CO^+)[14]; it comes from the fragmentation processes as follows:



$$\mathrm{\overset{CH_3}{\underset{C_5H_{11}O}{>}}C{=}\dot{O}^+} \begin{cases} \xrightarrow{\alpha} \mathrm{CH_3\dot{C}{=}\dot{O}^+ + C_5H_{11}\dot{O}} & \text{(a)} \\ \xrightarrow{\beta} \mathrm{CH_3\underset{\dot{O}}{\underset{|}{C}}{=}O + \dot{C}_5H_{10}^+ + H} & \text{(a')} \end{cases}$$

In the processes, (a) and (a′), mentioned above, α- and β-bond cleavages of the molecular ion may give the most important information on fragmentation processes. In the case of the low excess energy, when a β-bond cleavage occurs according to the (a′) process, the positive charge is localized on the alkyl group with a probability higher than the other fragments, because the $C_5H_{10}^+$ fragment ion is observed as the most intense peak. This discussions are based on the assumption of positive-charge migration in the ionized molecule.

According to the experimental results, the migration of the positive charge can be illustrated by the peak intensity ratio of the principal fragmentaions occurring from the following decomposition processes:

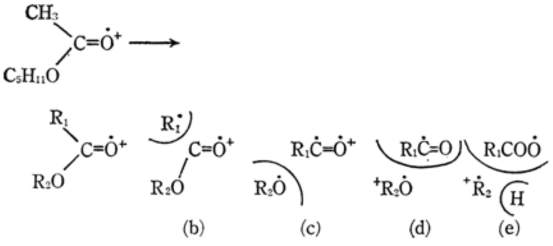


TABLE 3. RATIOS OF PRINCIPAL IONS AT PHOTON ENERGIES

Photon energy	$CH_3C{=}O^+ / C_5H_{10}^+$	$CH_3C{=}O^+ / C_5H_{11}O^+$	$C_5H_{11}O^+ / C_5H_{10}^+$
304 Å	2.	19	0.11
584 Å	0.43	4.7	0.09
1048 Å	0.17	2.5	0.06

The ions generated from the decompositions of (b) and (d) are generally weak, while both (c) and (e) are very intense peaks. As is shown in Table 3, the ratios of the CH_3CO^+ fragment ion to that of $C_5H_{10}^+$ with the three resonance lines mentioned above were 0.17, 0.43, and 2.0 respectively. This suggests that the CH_3CO^+ and $C_5H_{10}^+$ fragment ions are stable in a higher excess energy for the former and in a lower excess energy for the latter. For α- and β-bond cleavages (see (a) or (a′)), the ratios of the CH_3CO^+ fragment ion to that of $C_5H_{11}O^+$ were 2.5, 4.7, and 19 respectively. The ($C_5H_{11}O^+/C_5H_{10}^+$) ratio of the ions formed by the α- and β-bond cleavages are shown in the fourth column of Table 3. This value shows that the $C_5H_{10}^+$ ion produced from a β-bond cleavage is more stable than the $C_5H_{11}O^+$ ion, but the stability of the ion or the radical formed by the decomposition can not be exactly proved from the mass spectra at a low energy. The stabilization energy of the fragment resulting from the decomposition can be calculated by the ionization potentials of the molecule and radical.[15]

As has been mentioned above, the ($CH_3CO^+/C_5H_{10}^+$) or ($CH_3CO^+/C_5H_{11}O^+$) ratios are given a different value than the photon energies, since the positive charge in the ionized molecule is not localized especially on the atom of the molecule. The positive-charge migration in the ionized molecule, in general, can be explained in terms of the ionic resonance structures. For molecules including the carbonyl group, on the other hand, the ionization potential of the carbonyl molecule will be reduced by the effect of the electric charge flowing from the other part of the molecule.[16] In this case, the electron migration in the molecule can be illustrated by supposing inductive or mesomeric effects.

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[14] The ion peak with a mass of 43 is the doublet peak of $C_3H_7^+$ and CH_3CO^+ ions, and the ratio of the fragment ion, CH_3CO^+, to that of $C_3H_7^+$ changes as a function of the ionized energy. The ratios which are calculated from the high-resolution mass spectrum measured, using the ionizing electrons at 20, 30, 40 and 50 eV, are 0.08, 0.09, 0.10 and 0.12 respectively. The ratio gives a nearly constant value in the higher-ionizing-energy region.

[15] W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

[16] K. Higasi, I. Omura and H. Baba, *Nature*, **178**, 652 (1956).