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Mass Spectrometric Study of the Primary Processes in Photochemical Reactions. II. Mass Spectra of Methyl and Ethyl Radicals

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The mass spectra of methyl and ethyl radicals have been determined by the photolyses of methyl and ethyl iodide using a high intensity light beam and a collision-free photochemical reactor incorporated in the ion-source of a mass spectrometer. The parent ion peak was the most intense in the mass spectra of methyl and of ethyl radicals. Fair agreement was found between the present work and the result obtained by previous workers for pyrolytically produced methyl radicals.

In a previous work, the primary processes in 1,1′-azopropane photolysis were studied with a collision-free reactor incorporated in the ion source of a mass spectrometer.[1)] The photofragments produced were ionized by electron impact without their undergoing secondary processes and estimation of the primary processes was thus facilitated as compared with the conventional procedure of analysis of final reaction-products.

The primary step of the photolysis of 1,1′-azopropane was found to be composed of three competitive processes:

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \longrightarrow CH_3CH_2CH_2N_2CH_2 + CH_2CH_3 \qquad (1)$$

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \longrightarrow CH_3CH_2CH_2N_2 + CH_2CH_2CH_3 \qquad (2)$$

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \longrightarrow 2CH_3CH_2CH_2N \qquad (3)$$

As many as five kinds of photofragment radicals were formed in the primary step, and their assignments had to be made from the recorded mass spectrum of the photolyte mixture without any information on their cracking patterns. It is known that a large number of photochemical reactions consist of several competitive primary processes as in the case of 1,1′-azopropane. For analysis of the recorded mass spectrum of the photolyte mixture of photofragment radicals, it is desirable that the cracking patterns of the expected radicals are known before the experiment.

The mass spectra of free radicals have been measured only in a few cases.[2)] Only the parent-ion peaks of a number of free radicals were observed with the use of several kinds of reactors connected to the ion sources of mass spectrometers in the studies of free radicals produced by pyrolyses[3—6)] and of photochemical reactions.[7—9)]. It was thought to be worthwhile and of theoretical interest to measure the mass spectra of some frequently-appearing free radicals such as simple alkyl radicals, since several theoretical treatment have been reported for explaining the cracking pattern of the stable molecules.[10,11)] The theory could be extended to free radicals provided that suitable parameters are chosen for calculation.

In the present work, alkyl iodides were used for producing the corresponding alkyl radicals by photolyses. Since the C–I bond dissociation energies of alkyl iodides are much smaller than those of the C–C and C–H bonds,[12)] only the C–I bond rupture is expected in the primary step of the alkyl iodide photolysis.

Experimental

Methyl iodide and ethyl iodide(guaranteed-reagent grade, Tokyo Kasei Kogyo Co.) were purified by vacuum distillation.

The apparatus and method of operation were reported previously.[1)] The molecular flow of the reactant gas was supplied from a 5-1 reservoir kept in the dark into the reactor zone of the ion source through an orifice and a Pyrex glass gas-lead. The light source was a USH-500D 500W high-pressure mercury lamp(Ushio Electric Co.) and the light output was collimated in a housing fitted with a condensing lens system and a spherical mirror to obtain maximum intensity. The light flux was focused on the molecular flow of the reactant in the reactor through a quartz window fixed on a side-hole of the ion source of a Hitachi RMU-5 mass spectrometer. Considering the absorption spectra of methyl iodide and ethyl iodide in gas phase[13)] and the transmission of the Pyrex glass of the apparatus, the effective wavelength for the photolyses was estimated to be in the range 290—320 nm of the mercury-lamp output.

The mass spectrum obtained at 50 eV for each run was a superposition of the cracking patterns of the photofragments and that of unreacted alkyl iodide. The mass spectrum of the photofragment mixture was obtained after subtracting the contribution from unreacted alkyl iodide.

Results and Discussion

Mass spectrum of a photofragment mixture from the recorded mass spectrum is given in Table 1. By subtracting the contribution from unreacted methyl iodide from the recorded peak height, the residue Δ was obtained as the sum of the mass spectrum of each photofragment. Subtraction was done by normalizing at the mass number 142, the parent-ion peak of methyl iodide. Since all peaks can be attributed to CH_3 and I, it would be evident that only one primary process

TABLE 1. MASS SPECTRUM OF THE PHOTOLYTE FLOW OF METHYL IODIDE AT 50 eV
(in arbitrary units)

m/e	Peak height	Methyl iodide contribution	Δ	Assignment
12	1.1	0.8	0.3	CH_3
13	2.1	1.5	0.6	
14	5.3	3.6	1.7	
15	55.0	48.5	6.5	
127	60.5	55.2	5.3	I
142	150.5	150.5	—	methyl iodide

(4) is possible under the present conditions.

$$CH_3I + h\nu \longrightarrow CH_3 + I \qquad (4)$$

The mass spectrum of methyl radical obtained by averaging the results of nineteen runs is given in Table 2. The results of the present work are compared with those of Osberghaus and Taubert.[2] In both cases, the parent-ion peak was found to be the most intense and a fair agreement is obtained in relative abundance of the peaks at each mass number except for *m/e* 14. The discrepancy at *m/e* 14 might be caused by the difference between the procedure for methyl radical formation in the present work and that of Osberghaus and Taubert. In the latter, methyl radicals were produced by the pyrolysis of tetramethyl lead at 900 °C.

TABLE 2. MASS SPECTRUM OF METHYL RADICAL

m/e		12	13	14	15
Relative abundance	This work	5±2	11±6	25±8	100
	Osberghaus and Taubert	3	10	54	100

TABLE 3. MASS SPECTRUM OF THE PHOTOLYTE FLOW OF ETHYL IODIDE AT 50 eV
(in arbitrary units)

m/e	Peak height	Ethyl iodide contribution	Δ	Assignment
15	0.6	0.6	—	C_2H_5
25	0.5	0.4	0.1	
26	5.5	5.0	0.5	
27	30.0	24.9	5.1	
28	12.0	10.1	1.9	
29	39.0	33.7	5.3	
127	13.9	12.2	1.7	I
156	41.0	41.0	—	ethyl iodide

The mass spectrum of the photolyte flow of ethyl iodide is shown in Table 3. It can be seen that the procedure for obtaining it is the same as in the case of methyl iodide. Since the peak height at *m/e* 128 was found negligible in the residue Δ of each run, the process

$$C_2H_5I + h\nu \longrightarrow C_2H_4 + HI$$

could be neglected. Thus, only the following process is possible under the present experimental conditions.

$$C_2H_5I + h\nu \longrightarrow C_2H_5 + I \qquad (5)$$

The mass spectrum of ethyl radical obtained by averaging the results of twelve runs is shown in Table 4. In the mass spectrometric study of argon-ion bombardment on the ethylated surface of germanium,[14] occurrence of the fragment-ion from the liberated ethyl radicals by electron impact was suggested although the relative abundance of fragment-ion peak in the mass spectrum of ethyl radical was not determined because of the coexistence of other species emitted from the surface.

The peaks at *m/e* 12∼15 were not detected, indicating a negligible contribution of C–C bond rupture by electron impact of ethyl radical (Table 4).

Thus the results of the present work suggest that all the significant fragment-ions are produced solely by C–H bond rupture resulting from the electron bombardment at 50 eV both in the case of methyl and ethyl radicals. It is seen that the relative abundance of the fragment-ion is larger in the mass spectrum of C_2H_5 than in that of CH_3. The difference might be caused by the difference of excess energy partition in C_2H_5 and CH_3.

TABLE 4. MASS SPECTRUM OF ETHYL RADICAL

m/e	25	26	27	28	29
Relative abundance	1±1	13±3	82±12	44±10	100

The excess energy E_{exc} is expressed by the following equation:

$$\begin{aligned} E_{\mathrm{exc}} &= h\nu + E^{\mathrm{P}}_{\mathrm{int}} - D(\mathrm{C{-}I}) \\ &= E_{\mathrm{tr}} + E_{\mathrm{int}} \\ &= (E^{\mathrm{R}}_{\mathrm{tr}} + E^{\mathrm{I}}_{\mathrm{tr}}) + (E^{\mathrm{R}}_{\mathrm{int}} + E^{\mathrm{I}}_{\mathrm{int}}) \qquad (6) \end{aligned}$$

where, $h\nu$ is the photon energy, $E^{\mathrm{P}}_{\mathrm{int}}$ the initial parent molecule internal energy which is small, and D(C–I) the dissociation energy of the C–I bond. The excess energy is distributed in the total translational energy E_{tr} of alkyl radical R and iodine atom I and in the total internal energy E_{int} of both fragments.

In their photofragment spectroscopic study of the photodissociation of alkyl iodides, Riley and Wilson[15] pointed out that the ratio of $E^{\mathrm{R}}_{\mathrm{int}}$ appearing as the energy for alkyl-fragment internal excitation to the total energy $E^{\mathrm{R}}_{\mathrm{tot}}$ (translational and internal) given to alkyl fragment was found to be three times larger in C_2H_5 than in CH_3. It is plausible that the higher fraction of internal excitation can be one cause for the larger relative abundance of fragment-ion in the mass spectrum of ethyl radical as compared with methyl radical.

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