Mass Spectrometric Study of the Primary Processes in Photochemical Reactions. III. Primary Steps in Simple Ketone Photolysis and Mass Spectrum of Acetyl Radical

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The primary processes of the photolyses of acetone, methyl ethyl ketone, and methyl vinyl ketone have been studied using a high intensity UV light beam and collision-free photochemical reactor incorporated in the ion-source of a mass spectrometer. Photofragment radicals are directly detected from the mass spectrum of the photolyte flow and the primary processes are determined. Mass spectrum of acetyl radical has been obtained in addition to the mass spectra of hydrocarbon free radicals reported in previous papers. As for the ketones investigated, C–C bond rupture between acetyl and the remainder of the molecule is found predominant in the primary process of the photolysis in the region 290—320 nm.

The photolyses of simple ketones have been reported by many workers and the primary processes of these photochemical reactions have been studied on many compounds.[1] Most of the mechanisms, however, were proposed by the analyses of reaction products after the light-off of the experiments. Direct identification of the photofragments produced in the primary processes has been attempted and successful detections of free radicals from photolyses have been reported since the pioneering works in mass spectrometry[2] and in flash photolysis.[3] In most of the mass spectrometric studies for identification of free radicals in photochemical reactions, only the parent-ion peaks of free radicals have been detected.[4–6]

In the previous paper[7] photolysis of methyl and ethyl iodide was carried out using a light source incorporated in the ion-source of a mass spectrometer and the photofragments recorded in the mass spectrum were assigned to CH_3, C_2H_5, and I. The mass spectra of methyl and ethyl radicals thus obtained were in good agreement with the results of previous workers[8] and with theoretical estimation recently reported.[9]

In the present paper, the primary processes of the photolyses of acetone, methyl ethyl ketone and methyl vinyl ketone have been studied by direct identification of the primary photofragments from the mass spectra of photolyte mixtures.

In the case of these simple ketones, possible primary steps are as following since "Norrish Type II" process can be excluded because of the absence of γ-hydrogen atom:

$$CH_3COR + h\nu \longrightarrow CH_3CO + R \quad (1)$$
$$\longrightarrow CH_3 + COR \quad (2)$$
$$\longrightarrow CH_3 + R + CO \quad (3)$$

here, R denotes CH_3, C_2H_5, or C_2H_3 appropriately.

The purpose of the present paper is to detect directly the photofragments expected from processes (1)—(3) and thereby estimate the contribution from each process although the estimation has been reported by the previous workers[1] from the results of conventional analysis of final products.

Experimental

Acetone and methyl ethyl ketone obtained from Wako Pure Chemical Industry Ltd. and methyl vinyl ketone from Aldrich Chemical Co. were purified by vacuum distillation.

The apparatus and procedure were reported elsewhere.[7,10] The molecular flow of the reactant gas was supplied from a 5 l reservoir kept in the dark into the reactor installed in the ion-source of a Hitachi RMU-5 mass spectrometer 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 flux was focused on the molecular flow of the reactant in the reactor through a quartz window of the ion-source.

Considering the absorption spectra of the reactant ketones[1,11] and the transmission of the Pyrex glass of the reactor, the effective wavelength for 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 the unchanged reactant. The mass spectrum of the photofragment mixture was obtained by subtracting the contribution from unreacted reactant ketones.

Results and Discussion

Photolysis of Acetone. Table 1 shows an example of the mass spectrum of photolyte flow of acetone photolysis. By subtracting the contribution from unreacted acetone from the recorded peak height in the second column at each mass number, the residue Δ is obtained

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

m/e	Peak height	Acetone contribution	Δ
13	0.2	0.1	0.1
14	1.3	0.9	0.4
15	7.1	5.8	1.3
26	1.1	1.0	0.1
27	1.9	1.7	0.2
28	1.9	1.5	0.4
29	1.3	1.2	0.1
39	1.0	0.9	0.1
41	1.3	1.1	0.2
42	1.7	1.6	0.1
43	27.4	25.0	2.4
58	7.1	7.1	—

as the superposition of the mass spectrum of each photofragment.

The averaged value of Δ obtained from fifteen runs is shown in Table 2 where abundance is normalized at *m/e* 43. The peak height ratio at mass number 15, 14, and 13 is 55: 12: 6, which is equal to 100: 22: 11. This ratio is almost the same as the cracking pattern of methyl radical previously reported.[7] This means that the primary process of acetone photolysis at $\lambda > 290$ nm is almost exclusively the following one:

$$CH_3COCH_3 + h\nu \longrightarrow CH_3CO + CH_3 \qquad (4)$$

The above-mentioned observation is consistent with the results of previous works where the formation of acetyl radical was deduced by the static studies.[12]

Table 2. Mass spectrum of photofragment mixture of acetone photolysis

m/e	Abundance	Assignment
13	6±2	CH_3
14	12±4	
15	55±10	
26	7±3	CH_3CO
27	9±3	
28	12±3	
29	8±4	
39	7±3	
41	12±4	
42	9±3	
43	100	

In Table 2, the peaks at *m/e* 26, 27, 28, 29, 39, 41, 42, and 43 are assigned to acetyl radical. That is, peak *m/e* 43 is the base peak in the mass spectrum of acetyl radical and the cracking pattern coefficients of other peaks are shown.

Photolysis of Methyl Ethyl Ketone. Mass spectrum of the photofragment mixture of methyl ethyl ketone photolysis, which was obtained by subtracting the contribution of unreacted ketone from recorded mass spectrum in similar way to the case of acetone photolysis in Table 1, is shown in the second column of Table 3 in the form of relative abundance normalized at *m/e* 43. This abundance ratio is an average obtained from fifteen runs. The peaks *m/e* 43, 42, 41, and 39 are completely due to CH_3CO since the peak height ratio of these peaks is nearly the same as the cracking pattern of acetyl radical mentioned before. In the peaks *m/e* 29, 28, 27, and 26, there are partial contribution from acetyl radical. Since the cracking pattern of CH_3CO is known in Table 2, the residue Δ_1 is obtained by subtracting the contribution of CH_3CO.

In the residue Δ_1, the peaks *m/e* 26—29 may entirely be attributed to ethyl radical C_2H_5 since the peak height ratio in these mass numbers is close to the cracking pattern of C_2H_5 previously reported.[7] By subtracting the contribution of C_2H_5 from Δ_1, small residue Δ_2 is obtained. The peaks *m/e* 15 and 14 are due to CH_3, and *m/e* 57 peak may be assigned to photofragment C_2H_5CO.

Then, besides the major process (5)

$$CH_3COC_2H_5 + h\nu \longrightarrow CH_3CO + C_2H_5 \qquad (5)$$

Table 3. Mass spectrum of photofragment mixture of methyl ethyl ketone photolysis

m/e	Abundance	CH_3CO contribution	Δ_1	C_2H_5 contribution	Δ_2
14	4±2		4		4 (CH_3)
15	11±3		11		11
26	8±3	7	1	1	—
27	20±6	9	11	11	—
28	16±6	12	4	4	—
29	21±4	8	13	13	—
39	6±2	6	—		—
41	12±2	12	—		—
42	10±3	10	—		—
43	100	100	—		—
57	8±4		8		8 (C_2H_5CO)

the following process (6) is taken into account as a minor process in the primary step of methyl ethyl ketone photolysis in the wavelength range of this work:

$$CH_3COC_2H_5 + h\nu \longrightarrow CH_3 + C_2H_5CO \qquad (6)$$

The quantum yield ratio Φ_5/Φ_6 may be estimated to be 8.4 considering the total ion current ratio $[\sum I(CH_3CO) + \sum I(C_2H_5)]/[\sum I(C_2H_5CO) + \sum I(CH_3)]$ from Table 3 under the assumption of equal ionization cross section of each photofragment radical. Here, $\sum I(R)$ denotes the sum of all of the ion intensities originated from photofragment R.

Pitts and Blacet reported[13] that $\Phi_5/\Phi_6 = 40$ at 313 nm and $\Phi_5/\Phi_6 = 5.5$ at 265 nm by analyzing the final products in the photolysis of methyl ethyl ketone. Considering the effective wavelength range of 290—320 nm in the present work, the estimated Φ_5/Φ_6 value in this work is consistent with their results.

Photolysis of Methyl Vinyl Ketone. Primary process of the photochemical reaction of methyl vinyl ketone in gas phase seems to have not been explored although a number of works have been reported on the polymerization reaction.

An example of the mass spectrum of the photolyte flow of methyl vinyl ketone photolysis is shown in the second column of Table 4. By subtracting the contribution from unreacted methyl vinyl ketone, the residue Δ_1 is obtained as a superposition of the ion current from each photofragment. The residue Δ_2 is obtained by subtracting the CH_3CO contribution from Δ_1. Since the most intense peak in Δ_2 is found at *m/e* 27, the mass number of the base peak in the mass spectrum of vinyl radical recently reported,[14] the contribution from C_2H_3 is subtracted from Δ_2 resulting in the small residue Δ_3.

Because of the small peaks in Δ_3, the minor process (8) is considered although major process is evidently process (7) in the primary step of methyl vinyl ketone photolysis:

$$CH_3COC_2H_3 + h\nu \longrightarrow CH_3CO + C_2H_3 \qquad (7)$$

$$CH_3COC_2H_3 + h\nu \longrightarrow C_2H_3CO + CH_3 \qquad (8)$$

In the residue Δ_3, the peak *m/e* 15 suggests the formation of CH_3 and the peak *m/e* 55 may be due to C_2H_3CO. Small peaks at *m/e* 39 and 42 are presumably the frag-

TABLE 4. MASS SPECTRUM OF PHOTOFRAGMENT MIXTURE OF METHYL VINYL KETONE PHOTOLYSIS

m/e	Peak height	$CH_3COC_2H_3$ contribution	Δ_1	CH_3CO contribution	Δ_2	C_2H_3 contribution	Δ_3
14	2.1	2.1	—		—		—
15	5.3	5.1	0.2		0.2	0.1	0.1
26	3.4	3.2	0.2	0.1	0.1	0.1	—
27	11.4	10.2	1.2	0.1	1.1	1.1	—
28	1.7	1.6	0.1	0.1	—		—
39	1.7	1.5	0.2	0.1	0.1		0.1
41	1.3	1.2	0.1	0.1	—		—
42	2.3	2.1	0.2	0.1	0.1		0.1
43	13.4	12.6	0.8	0.8	—		—
55	16.1	15.8	0.3		0.3		0.3
70	6.2	6.2	—		—		—

ment ions from C_2H_3CO. As for the mass spectra of free radicals previously studied,[7,8,14] the parent-ion peak is always the most intense base peak.

The reproducibility in the mass spectrum of the photolyte flow is poor in the photolysis of methyl vinyl ketone compared with the case of acetone and methyl ethyl ketone under the present experimental conditions probably because of some deposit on the reactor wall, although the predominance of process (7) over process (8) is always found in every run of methyl vinyl ketone photolysis. The contribution ratio (7)/(8) may roughly be estimated about 10.

Summary. As for the simple ketones studied in this work, the following process (I) producing acetyl radical is always found predominant in the primary step of the photolysis of these ketones by mass spectrometric detection of photofragment radicals:

$$CH_3COR + h\nu \longrightarrow CH_3CO + R \qquad (I)$$

$$(R = CH_3,\ C_2H_5 \text{ and } C_2H_3)$$

In the case of methyl ethyl ketone and methyl vinyl ketone, the minor process (II) is found by the detection of CH_3 and RCO:

$$CH_3COR + h\nu \longrightarrow CH_3 + RCO \qquad (II)$$

The predominance of process (I) over (II) might be due to the high stability of acetyl radical whose heat of formation is known to be −11 kcal/mol.[15]

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