BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2290—2292 (1973)

Mass Spectrometric Study of the Primary Processes in Photochemical Reactions I. Photodecomposition of 1,1′-Azopropane

Shigeru YAMASHITA and Teruo HAYAKAWA
Department of Chemistry, Faculty of Liberal Arts and Sciences, University of Osaka Prefecture,
Mozu-Umemachi, Sakai, Osaka 591

(Received January 11, 1973)

Primary processes of the photolysis of 1,1′-azopropane were studied using a high intensity light beam and a collision-free photochemical reactor incorporated in the ion-source of a mass spectrometer. The photofragments produced by the following three one-bond fission primary processes were found.

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \longrightarrow CH_3CH_2CH_2N_2CH_2 + CH_2CH_3 \tag{1}$$

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \longrightarrow CH_3CH_2CH_2N_2 + CH_2CH_2CH_3 \tag{2}$$

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \longrightarrow 2\,CH_3CH_2CH_2N \tag{3}$$

The lifetime of these photofragments seems to be longer than 50 μs considering the experimental conditions.

Several mass spectroscopic instruments have been reported for the study of primary processes of photochemical reactions. The essential part of these instruments is the photolysis reactor connected with the ion source of the mass spectrometer for prompt detection of photofragments produced in the primary processes.[1–4] Information has been obtained for many reaction systems.

However, in these mass spectroscopic intruments, collision of the photofragments with each other and with the reactor wall is inevitable. Most reaction products detected were molecular species and a few free radicals in certain cases.[5–7]

One of us reported on the photolysis of mercaptans and alkyl sulfides with a mass spectrometer connected with a fast-flow reactor.[8,9] We were interested in the use of molecular flow of reactant in the photolysis reactor involved in the ion source of the mass spectrometer. A mass spectrometric investigation of the primary processes in the photolysis of 1,3-butadiene with a pulsed flash-lamp and the molecular beam of the reactant vapor was reported by Bergmann and Demtröder.[10]

We attempted the use of steady illumination with a high-intensity light beam and the molecular flow type gas-lead of a Pyrex glass tube in the ion source of a mass spectrometer for studying primary processes of photochemical reactions.

From an interest in re-examination of the primary processes of 1,1′-azopropane, we carried out the photolysis of azopropane using the above instrument. The present paper describes the results.

The primary process was found to be[11]

$$CH_3CH_2CH_2N{=}NCH_2CH_2CH_3 + h\nu \longrightarrow 2\,CH_3CH_2CH_2 + N_2 \tag{a}$$

indicating simultaneous two-bond-splitting. Gowenlock *et al.* pointed out the possibility of the single bond-splitting process in their electron impact study of azo-*n*-alkanes,[12] suggesting that the products ($2\,CH_3CH_2CH_2+N_2$) in process (a) might be derived from a preceding state ($CH_3CH_2CH_2N_2+CH_3CH_2CH_2$).

We expected to find photofragments such as $CH_3CH_2CH_2N_2$ produced by single bond-rupture with a collision-free reactor incorporated in the ion source of the mass spectrometer. Collisions during the time between the photon impact and the detection of the photofragments could be neglected provided that the experimental conditions for the molecular flow of the reactant were satisfied by use of proper arrangement of gas-leak orifice and reservoir pressure.

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Experimental

Figure 1 shows a schematic diagram of the photolysis reactor and ion source. The mass spectrometer was a modified Hitachi RMU-5 type instrument, the ion current being detected by a ten-stage secondary electron multiplier.

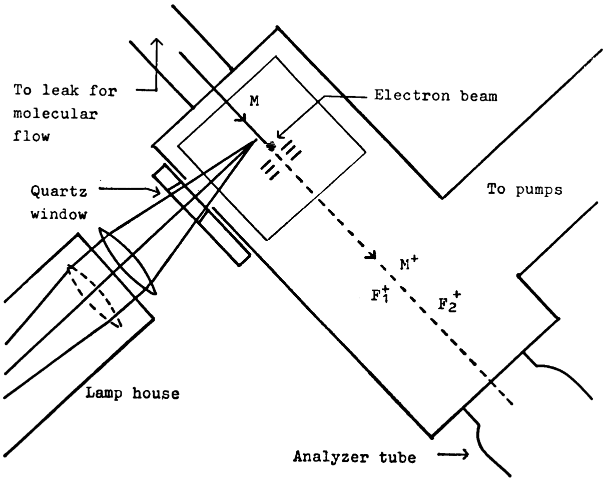

Fig. 1. Illustration of the reactor in the ion source.
M means the reactant azopropane, M^+ denotes the ion from unreacted azopropane and F_1^+, F_2^+ show the ions from the photofragments.

Molecular flow of the reactant azopropane was supplied from a 5-l gas reservoir kept in the dark into the ion source through an orifice and a Pyrex glass gas-lead. The pressure in the reactor was about 10^{-5} Torr.

The light source for the photolysis was a USH-500D 500W high-pressure mercury lamp (Ushio Electric Co.). The light output was collimated in a housing fitted with a condensing lens system and a spherical mirror to obtain maximum intensity. The total light flux was estimated by ferrioxalate actinometer to be about 3×10^{18} quanta/s. The light flux from the lamp house was focused on the molecular flow of the reactant in the Pyrex gas-lead tube through a quartz window fixed on a side hole of the ion source block. In order to cut off wavelengths shorter than 300 nm, a Toshiba UV-29 filter was installed before the quartz window. Most of the incident light-quanta into the reactor were of 365 nm with small contribution from that of 334 nm. No light-exit window[10] was installed in this work, but the effect of scattered light was considered insignificant because of the fact that several metal pieces of the ionization chamber effectively shield the scattered light.

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

For detecting the signal of the photofragments, sufficient concentration of the photofragments relative to that of unreacted azopropane was necessary. This could be achieved by using a highly intense light beam focused on the molecular flow of the reactant and by using a reactant with a very high molecular extinction coefficient in the wavelength range of the light source. Since azopropane has absorption in near ultraviolet (Fig. 2), the high-intensity mercury lamp was proved to be effective for detecting the photofragments from azopropane.

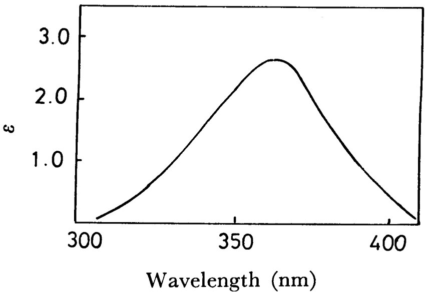

Fig. 2. Absorption spectrum of 1,1'-azopropane $CH_3CH_2CH_2NNCH_2CH_2CH_3$ (gas phase).

Results and Discussion

The procedure to obtain the mass spectrum of the photofragment mixture from the recorded mass spectrum is given in Table 1. By subtracting the contribution from unreacted azopropane (third column) from the recorded peak height (second column), we obtain the residue Δ, the sum of the mass spectrum of the photofragments. Only the residues of significant magnitude are shown. Subtraction was done by normalizing at the mass number 114, the parent peak of azopropane.

Table 1. Mass spectrum of the photolyte flow of 1,1'-azopropane
(in arbitrary units)

m/e	Peak height	Azopropane contribution	Δ	Assignment
27	7.5	6.4	1.1	
28	75.0	75.0	—	
29	46.5	37.2	9.3	C_2H_5
30	14.0	13.0	1.0	
39	26.3	27.2	—	
41	99.0	97.4	1.6	
42	27.1	25.2	1.9	
43	239.5	231.0	8.5	C_3H_7
56	3.8	3.0	0.8	
57	5.6	3.1	2.5	C_3H_7N
71	7.9	6.9	1.0	$C_3H_7N_2$
85	2.1	1.6	0.5	$C_3H_7N_2CH_2$
114	20.0	20.0	—	Azopropane

The residue at *m/e* 28 was found to be negligible, indicating that N_2 was not a primary product. Some process preceding (a) might be expected.

The residues at *m/e* 85, 71 and 57 (Table 1) could be assgined as the ion peaks of $CH_3CH_2CH_2N_2CH_2$, $CH_3CH_2CH_2N_2$ and $CH_3CH_2CH_2N$, respectively. Presumably these photofragment radicals were produced in the following primary processes:

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \rightarrow CH_3CH_2CH_2N_2CH_2 + CH_2CH_3 \quad (1)$$

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \rightarrow CH_3CH_2CH_2N_2 + CH_2CH_2CH_3 \quad (2)$$

$$CH_3CH_2CH_2N_2CH_2CH_2CH_3 + h\nu \rightarrow 2\ CH_3CH_2CH_2N \quad (3)$$

TABLE 2. MASS SPECTRA OF THE PHOTOFRAGMENT MIXTURES

m/e	27	28	29	30	39	41	42	43	56	57	71[a]	85
Run 1	0.6	—	7.0	2.5	1.3	—	3.6	4.8	0.5	0.4	1.0	0.1
Run 2	0.6	—	8.0	0.6	—	—	3.0	—	0.4	1.0	1.0	0.8
Run 3	0.3	—	4.5	2.0	2.5	0.7	1.2	2.0	0.2	0.7	1.0	0.2
Run 4	—	—	2.1	1.9	2.6	0.1	2.6	2.4	0.3	0.9	1.0	0.1
Run 5	0.5	—	5.8	1.9	—	1.5	1.1	12.5	0.6	1.4	1.0	0.1
Run 6	1.1	—	9.3	1.0	—	1.6	1.9	8.5	0.8	2.4	1.0	0.5
Run 7	1.5	—	12.8	3.8	3.2	2.3	6.0	4.4	0.9	0.6	1.0	0.3

a) Peak heights are normalized to unity at *m/e* 71.

The ion peak at m/e 43 was due to the unreacted azopropane whose concentration is several tens of times higher than the sum of the concentration of photofragments. Thus fluctuation of the peak height of *m/e* 43 affected its Δ-value of photofragments to such an extent to make it unreliable.

The residues at lower mass numbers were taken for mass spectral fragment ion peaks of the primary photofragments induced by electron impact. There was contribution from the ions of the photofragments $CH_3CH_2CH_2$ and CH_3CH_2 at *m/e* 43 and 29.

The results are summarized in Table 2, where the peak heights are normalized to unity at *m/e* 71. Assuming the same sensitivity for the three of photofragments of the mass numbers 85, 71 and 57, the probability of the occurrence of the primary processes (1), (2) and (3) seems to be approximately comparable with each other.

From the geometry of the instrument and the experimental conditions, the lifetime of these photofragments seems to be longer than 50 μs.