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Photodecomposition of Vinyl Iodide in Gas Phase

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Photodecomposition of vinyl iodide has been studied at 313 and 254 mμ using a high intensity light source. Because of high concentration of the radicals formed primarily due to the high intensity of the light source, only the inter-radical reactions were taken into account in considering the secondary processes.

Both molecular and free radical processes have been observed in the primary process and the ratio of the contribution of molecular process to free radical process was found to be about 1 : 6 in the wavelength range studied. A slight energy dependence of k_d/k_c, the ratio of the rate of disproportionation reaction to that of combination reaction of vinyl radicals, was found in the secondary processes.

The primary process of the photochemical reaction has been studied by many investigators using various instruments for the detection of short-lived intermediates produced in the process.[1)]

In the case of photochemical studies carried out by means of a conventional static reactor and the analysis of the final products, there are ambiguities due to the contributions from so many secondary processes, most of which are the reactions between primary fragment radicals and reactant molecules since the concentration of the primary fragment is usually much lower than that of the reactant molecules.

By use of a high intensity light source in the study of photochemical reactions, the reaction scheme would be simplified even in the conventional static method

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1) R. G. W. Norrish and G. Porter, *Nature*, **164**, 658 (1949). G. Porter, *Proc. Roy. Soc.*, **A200**, 284 (1950). G. Herzberg and D. A. Ramsay, *Proc. Roy. Soc.*, **A233**, 34 (1955). F. P. Lossing, D. G. H. Harsden, and J. B. Farmer, *Can. J. Chem.*, **34**, 701 (1956). G.B. Kistiakowsky and P.H. Kydd, *J. Amer. Chem. Soc.*, **79**, 4825 (1957). K. Bergman and W. Demströder, *J. Chem. Phys.*, **48**, 18 (1968).

excluding radical-molecule reactions because of the high concentration of the reactive primary fragment radicals. In the photochemical studies of azoalkanes[2] and alkyl sulfides[3] using high intensity light sources, only the products from the reactions between the free radicals formed in the primary processes were observed. Since the products from the free radical-reactant molecule reactions were not detected in these works, the reaction schemes were rather simplified.

Although a number of data are available for the reactions of alkyl radicals, comparatively few studies have been carried out on the reactions of unsaturated free radicals.[4,5,6]

In the present work, direct photolysis of vinyl iodide in the gas phase at room temperature has been studied under high light intensity conditions. Photolysis of vinyl iodide was reported by Roberge and Herman.[7] However, the study was carried out in carbon tetrachloride solution with a light source of rather low intensity.

The purpose of the present paper was to find the primary process in the photodecomposition of vinyl iodide and to study the energy dependence of the primary and secondary processes by changing the wavelength of the exciting light.

Experimental

Vinyl iodide was prepared by the reaction of 1,2-diiodoethane with sodium ethoxide[8] and purified by vacuum distillation. Before every run, the sample was cautiously degassed at the temperature of liquid nitrogen. The absorption spectrum of vinyl iodide vapor is shown in Fig. 1. The reactor was a conventional drum-type quartz cylinder. The light source was a USH-500D 500W high pressure mercury lamp manufactured by Ushio Electric Co. and the light output was collimated in a housing fitted with condensing lens system and spherical mirror to obtain maximum intensity. The total light flux projected to the surface of the reactor was estimated by ferrioxalate actinometer[9] to be about 3×10^{18} quanta/sec, which is as high as the intensity of the light sources used by previous workers.[2,3]

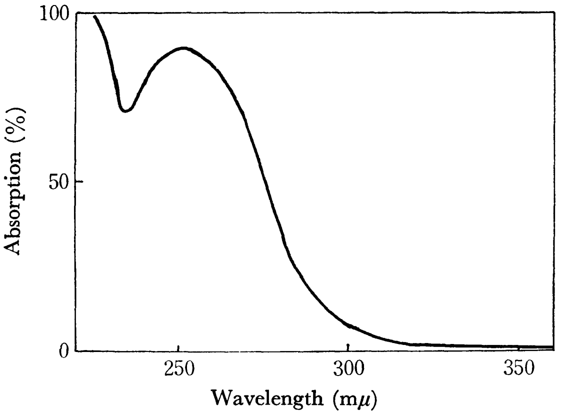

Fig. 1. Absorption spectrum of vinyl iodide vapor. Pressure; 60 torr. Path length; 50 mm.

The reactant gas was irradiated at room temperature in order to exclude thermal reactions. One series of the experiments was carried out using a Toshiba UV-29 filter which transmits a light of wavelength greater than 290 $m\mu$. In the other series, the sample in the reactor was irradiated by a full arc with no filter.

In the UV-29 series experiments, the most abundant quanta absorbed by vinyl iodide are those from the 313 $m\mu$ output of the mercury lamp considering the absorption curve of vinyl iodide and other experimental conditions.

In the full arc series experiments, it was not easy to estimate the most effective radiation because of the lack of detailed energy distribution data of the lamp in the wavelength range smaller than 300 $m\mu$. By rough estimation, however, the most effective wavelength in the full arc experiments seems to be 254 $m\mu$ line from the mercury lamp. The conversion of the reactant was less than 5% in all runs. Since the dissociation energy of C-I bond in vinyl iodide has been reported to be 66.5 kcal/mol,[10] the light quanta have enough energy for C-I bond rupture both in UV-29 and full arc series. Before the analysis of the reaction products, unreacted vinyl iodide and non-volatile products were condensed by a cold trap cooled at −79°C. The separated volatile products were analyzed by gas chromatograph with a column packed with dimethylsulfolane on alumina and by a Hitachi RMU-5 mass spectrometer.

Results and Discussion

The main products in both UV-29 and full arc series experiments were ethylene, acetylene and 1,3-butadiene. Hydrogen iodide in the reaction products was detected by mass spectrometry. Iodine formation was observed spectrophotometrically by dissolving a small amount of non-volatile products deposited on the reactor wall into *n*-hexane solution. Quantitative de-

Table 1. Photolysis of vinyl iodide

CH_2=CHI (Torr)	Products (micromole)		
	C_2H_4	C_2H_2	C_4H_6
9.26	0.28	0.40	0.07
15.35	0.37	0.53	0.15
22.39	0.51	0.85	0.31
33.70	0.46	0.69	0.36
35.33	0.50	0.75	0.36
40.13	0.49	0.73	0.45
40.47	0.52	0.84	0.45
48.15	0.51	0.68	0.40

Light source; high pressure mercury lamp with a Toshiba UV-29 filter.
Irradiation; 14 min.

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[2] J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **45**, 2327 (1967).

[3] S. Yamashita and F. P. Lossing, *ibid.*, **46**, 2925 (1968). A. Jones, S. Yamashita, and F. P. Lossing, *ibid.*, **46**, 833 (1968).

[4] N. A. Weir, *J. Chem. Soc.*, (**1965**) 6870.

[5] D. J. LeRoy and A. W. Tickner, *J. Chem. Phys.*, **19**, 1247 (1951).

[6] A. G. Sherwood and H. E. Gunning, *J. Phys. Chem.*, **69**, 2323 (1965). M. G. Bellas, J. K. S. Wan, W. F. Allen, P. O. Strausz, and H. E. Gunning, *ibid.*, **68**, 2170 (1964).

[7] P. C. Roberge and J. A. Herman, *Can. J. Chem.*, **45**, 1361 (1966).

[8] J. Spence, *J. Amer. Chem. Soc.*, **55**, 1290 (1933).

[9] C. A. Parker, *Proc. Roy. Soc.*, **A235**, 518 (1956).

[10] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities", St Martin's Press, New York, N. Y. (1966), p. 63.

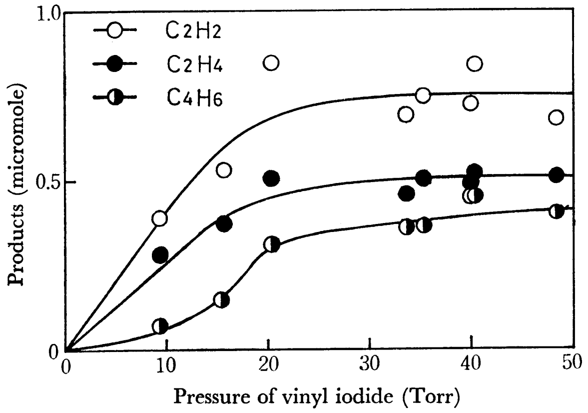

Fig. 2. Pressure dependence of the products formation in vinyl iodide photolysis. Filter; Toshiba UV-29. Irradiation; 14 min.

termination of hydrogen iodide and iodine could not be achieved. The rather poor material balance of carbon and hydrogen in the reaction products might be caused by missing hydrogen iodide and a trace of polymeric products in the quantitative determination.

The results of the UV-29 series experiments at various initial pressures of vinyl iodide are shown in Table 1 and Fig. 2. In the pressure range lower than 20 torr, it is seen that the formation of C_2H_2 and C_2H_4 is proportional to the pressure of vinyl iodide and that of 1,3-butadiene to the square of vinyl iodide pressure. Saturation of the product formation takes place in high pressure range. This seems to be due to the fact that the transparency of the reactor wall decreases rapidly in the high pressure runs by the deposition of trace of opaque produsts, probably polymeric, on the reactor wall.

Table 2. Photolysis of vinyl iodide

CH_2=CHI (Torr)	Products (micromole)		
	C_2H_4	C_2H_2	C_4H_6
4.63	0.87	1.06	0.13
6.04	1.17	1.59	0.19
8.67	1.38	2.20	0.37
10.84	1.54	2.63	0.40
13.49	1.61	2.72	0.37
15.20	1.22	2.81	0.46
29.74	0.94	1.59	0.30
35.55	1.07	1.45	0.28
38.59	1.03	1.48	0.31

Light source; full arc of high pressure mercury lamp.
Irradiation; 4 min.

The results of the full arc series are shown in Table 2 and Fig. 3. The results were less reproducible than in the case of the UV-29 series.

These results of high intensity photolyses were expected to differ from those obtained by conventional low intensity light source.

The results obtained with the use of low intensity light source are shown in Table 3 together with those obtained with high intensity source for comparison. The composition of the two reaction products differs.

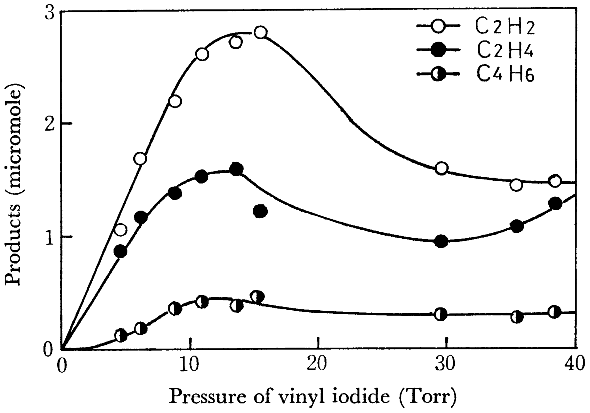

Fig. 3. Pressure dependence of the products formation in vinyl iodide photolysis by full arc without filter. Irradiation; 4 min.

Table 3. Comparison of the composition of the products in high intensity photolysis of vinyl iodide with the results of low intensity photolysis

	CH_2=CHI (Torr)	Products (micromole)		
		C_2H_4	C_2H_2	C_4H_6
High intensity photolysis	19.40	0.58	1.32	0.52
	24.28	0.73	1.58	0.90
	31.73	0.78	1.66	1.21
Low intensity photolysis	30.71	0.32	0.13	0.03
	30.12	0.32	0.12	0.04
	30.04	0.29	0.15	0.04

Light source for high intensity experiments was a USH-500 high pressure mercury lamp whose incident flux to the reactor was of the order 10^{18} photons/sec.

Light source for low intensity experiments was a SHL-100UV high pressure mercury lamp whose incident flux to the reactor was of the order 10^{16} photons/sec.

Filter; Toshiba UV-29 for both series experiments.

Irradiation time was adjusted for obtaining the products of the same order of amount in the two series.

In contrast to high intensity experiments, the predominant product in low intensity experiments is ethylene as reported by previous workers,[7] indicating that the hydrogen abstraction by vinyl radical-vinyl iodide molecule reaction is more predominant than radical-radical reaction in the low intensity condition because of the low concentration of vinyl radicals.

When nitric oxide was added to the reaction mixture, production of C_2H_4 and C_4H_6 was quenched completely whereas C_2H_2 formation was partly suppressed. The effect of nitric oxide suggests that C_2H_4 and C_4H_6 are formed from free radicals produced in a primary process. On the other hand, C_2H_2 seems to be produced by molecular process as well as by free radical process since its formation was not completely quenched by the addition of the free radical quencher nitric oxide.

It was confirmed that the rate of decomposition was proportional to light intensity as shown in Fig. 4, which means that the reaction rate is proportional to the number of quanta absorbed by the reactant molecules.

Thus, the primary steps of the photodecomposition of vinyl iodide under the conditions of the present work are supposed to be as follows:

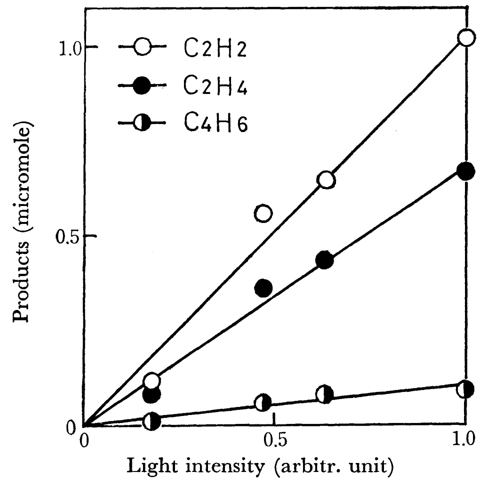

Fig. 4. The effect of light intensity on the products formation.

$$C_2H_3I + h\nu \longrightarrow C_2H_3I^* \qquad (1)$$

$$C_2H_3I^* \xrightarrow{k_1} C_2H_3\cdot + I \qquad (2)$$

$$C_2H_3I^* \xrightarrow{k_2} C_2H_2 + HI \qquad (3)$$

where, the rate of process (1) is approximately expressed by $k_0I_0[C_2H_3I]$, which means that it is proportional to light intensity I_0 and to the pressure of the reactant $[C_2H_3I]$. Process (2) is a free radical process and process (3) a molecular process where the products are molecular species.

Because of the high intensity of the light source, radical-molecule reactions could be neglected in the secondary processes following the primary processes (1), (2), and (3).

The reaction scheme for the secondary processes can be proposed as follows:

$$2C_2H_3\cdot \xrightarrow{k_d} C_2H_2 + C_2H_4 \qquad (4)$$

$$2C_2H_3\cdot \xrightarrow{k_r} C_4H_6^* \qquad (5)$$

$$C_4H_6^* \xrightarrow{k_{-r}} 2C_2H_3\cdot \qquad (6)$$

$$C_4H_6^* + M \xrightarrow{k_s} C_4H_6 + M \qquad (7)$$

$$I + I + M \longrightarrow I_2 + M \qquad (8)$$

where $C_4H_6^*$ denotes a vibrationally excited complex.

The study of mercury-photosensitized reaction of vinyl chloride in the gas phase by Gunning and his co-workers[6] is instructive for the present work although the reactants and the experimental conditions are different. The process of vinyl radical formation by the reaction of Hg(6 $^3P_1$) atoms with vinyl halide can be ruled out for direct absorption excitation of the reactant molecule. Vinyl radical formation is given by process (2). The hydrogen-abstraction process

$$C_2H_3\cdot + C_2H_3I \longrightarrow C_2H_4 + C_2H_2I$$

can be ruled out because of the high concentration of C_2H_3 radicals since radical-radical reaction is much faster under such conditions. In contrast of the results of Gunning and co-workers the value of the ratio $[C_2H_4]/[C_2H_2]$ was time-independent. The reaction scheme is thus not incompatible with their results,[6] if we consider the difference in experimental conditions.

The contribution of the process

$$C_2H_3\cdot + I \longrightarrow C_2H_3I$$

was assumed to be negligible compared to reactions (4) and (5) by analogy with the fact that the rate constant of the recombination process

$$R\cdot + R\cdot \longrightarrow R\text{-}R$$

is about 10^2 times larger than that of the process

$$R\cdot + X \longrightarrow R\text{-}X$$

where R denotes alkyl radicals and X means NO molecule.[11] Assuming the short life of $C_2H_3I^*$ as in the case of CH_3Cl^*,[6] contribution of the process

$$C_2H_3I^* + M \longrightarrow C_2H_3I + M$$

might be smaller than processes (2) and (3).

The hydrogen-abstraction reaction by iodine atom could be excluded because of its low reaction rate.

Considering the dissociation energy of the C–I bond in vinyl iodide and the energy level of the lowest excited state of iodine atom which is known to be 21.7 kcal/mol,[12] contribution of the electronically excited iodine atom can not be excluded in UV-29 and full arc series while most of the excess energy at the C–I bond rupture would be distributed to the lighter fragment[13] $C_2H_3\cdot$.

Applying the steady state method, the rates of formation of C_2H_2, C_2H_4, and C_4H_6 are expressed as follows:

$$\frac{d[C_2H_2]}{dt} = \frac{I_0k_0k_2}{k_1+k_2}[C_2H_3I] + \frac{I_0k_0k_1k_d(k_s[M]+k_{-r})[C_2H_3I]}{2(k_1+k_2)\{(k_d+k_r)(k_s[M]+k_{-r})-k_rk_{-r}\}} \qquad (9)$$

$$\frac{d[C_2H_4]}{dt} = \frac{I_0k_0k_1k_d(k_s[M]+k_{-r})[C_2H_3I]}{2(k_1+k_2)\{(k_d+k_r)(k_s[M]+k_{-r})-k_rk_{-r}\}} \qquad (10)$$

$$\frac{d[C_4H_6]}{dt} = \frac{I_0k_0k_1k_rk_s[M][C_2H_3I]}{2(k_1+k_2)\{(k_d+k_r)(k_s[M]+k_{-r})-k_rk_{-r}\}} \qquad (11)$$

Assuming the constancy of $d[C_2H_2]/dt$, $d[C_2H_4]/dt$, and $d[C_4H_6]/dt$ in the low conversion period, the following equation is obtained:

$$\frac{[C_2H_2]+[C_4H_6]}{[C_2H_4]+[C_4H_6]} = 1 + \frac{2k_2}{k_1} \qquad (12)$$

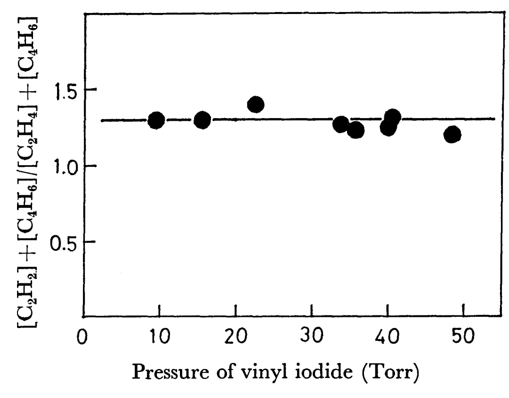

Fig. 5. Reaction product ratio $[[C_2H_2]+[C_4H_6]]/[[C_2H_4]+[C_4H_6]]$ obtained at various pressures of vinyl iodide. Filter; Toshiba UV-29.

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11) K. J. Laidler, "Chemical Kinetics", Mc-Graw-Hill Co., New York, N. Y., p. 184 (1965).

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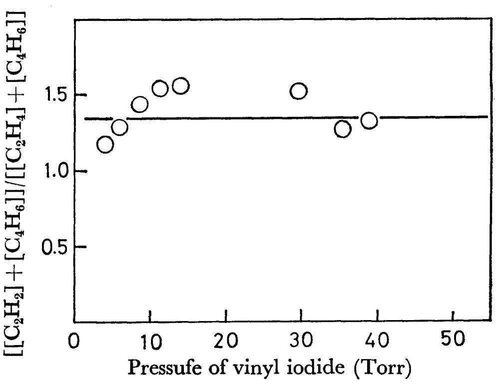

Fig. 6. Reaction product ratio $[[C_2H_2]+[C_4H_6]]/[[C_2H_4]+[C_4H_6]]$ obtained at various pressures of vinyl iodide when full arc was used without filter.

Table 4. Contribution of molecular and radical processes in the photodecomposition of vinyl iodide

Experiment	Molecular process	Radical process	k_2/k_1	Most effective wavelength for excitation
UV-29 series	13±2%	87±2%	0.14± 0.02	313 mμ (91 kcal/mol)
Full arc series	17±5%	83±5%	0.20± 0.07	254 mμ (112 kcal/mol)

The equation shows that the reaction product ratio $([C_2H_2]+[C_4H_6])/([C_2H_4]+[C_4H_6])$ is constant and k_2/k_1 value can be obtained.

It is seen in Figs. 5 and 6 that the ratio $[[C_2H_2]+[C_4H_6]]/[[C_2H_4]+[C_4H_6]]$ is constant in both UV-29 and full arc series although the results are rather scattered in the latter. Table 4 shows that the ratio k_2/k_1, ratio of the contribution of molecular process (3) to free radical process (2) in the primary processes, is about 1/6 and almost independent of the exciting energy in the range 91—112 kcal/mol.

The quantum yield for the sum of molecular and radical processes was found to be 0.26±0.2 in the UV-29 series.

In the low pressure range, where $k_s[M] \ll k_{-r}$, Eqs. (9), (10), and (11) are respectively reduced to

$$\frac{d[C_2H_2]}{dt} = \frac{(k_1+2k_2)k_0I_0}{2(k_1+k_2)}[C_2H_3I] \tag{13}$$

$$\frac{d[C_2H_4]}{dt} = \frac{k_0k_1I_0}{2(k_1+k_2)}[C_2H_3I] \tag{14}$$

$$\frac{d[C_4H_6]}{dt} = \frac{k_0k_1k_rk_sI_0}{2(k_1+k_2)k_dk_{-r}}[C_2H_3I]^2 \tag{15}$$

These equations explain the results in which, in the low pressure range, the rates of ethylene and acetylene formation are proportional to the pressure of vinyl iodide, while the rate of 1,3-butadiene formation is proportional to the square of vinyl iodide pressure.

From Eqs. (14) and (15) we obtain

$$\frac{[C_4H_6]}{[C_2H_4]} = \frac{k_rk_s}{k_dk_{-r}}[C_2H_3I] \tag{16}$$

This means that the product ratio $[C_4H_6]/[C_2H_4]$ is proportional to the pressure of vinyl iodide in the low pressure range as shown in Fig. 7.

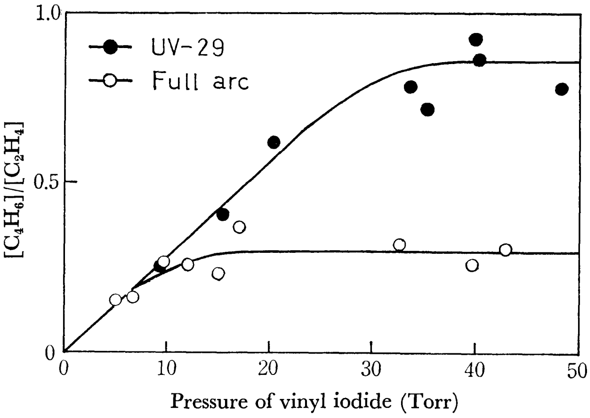

Fig. 7. Linear relation between the ratio $[C_4H_6]/[C_2H_4]$ and vinyl iodide pressure in low pressure range.

From Eqs. (10) and (11), the following equation is obtained:

$$\frac{[C_2H_4]}{[C_4H_6]} = \frac{k_d}{k_r}\left(1+\frac{k_{-r}}{k_s}\cdot\frac{1}{[M]}\right) \tag{17}$$

This shows the linear relation between the ratio $[C_2H_4]/[C_4H_6]$ and $1/[M]$ where $[M]$ denotes the pressure of the reactant. Fig. 8 shows that the linear relation holds both for UV-29 and full arc series. From Fig. 8, the value of the ratio k_d/k_r is found to be 0.43 in UV-29 series and 2.5 for full arc experiments.

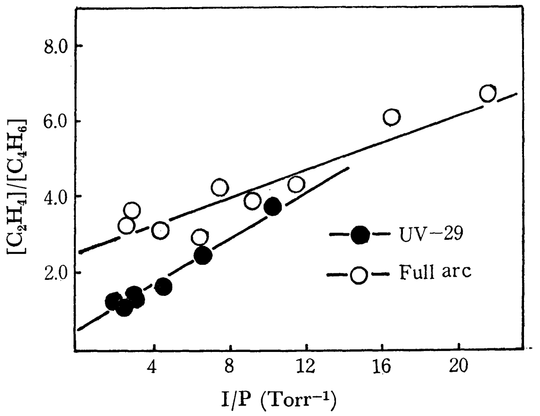

Fig. 8. Linear relation between the ratio $[C_2H_4]/[C_4H_6]$ and the reciprocal of vinyl iodide pressure.

Table 5. The ratio of k_d/k_c for vinyl radical presented by different works

k_d/k_c	Method	Investigators
0.4	Photodecomposition of vinyl iodide mostly at 313 mμ	S. Y. *et al.*
2.5	Photodecomposition of vinyl iodide mostly at 254 mμ	S. Y. *et al.*
1.1	Irradiation of the mixture of vinyl formate and acetaldehyde at a wavelength greater than 300 mμ	N. A. Weir; ref. 4
2	Decomposition of the mixture of vinyl iodide and vinyl bromide by sodium diffusion flame technique	D. J. LeRoy and A. W. Tickner; ref. 5
0.05	Photodecomposition of mercury divinyl by 220—260 mμ	A. G. Sherwood and H. E. Gunning; ref. 6

The value k_d/k_c which is usually used for the rate constant ratio of disproportionation to combination of the radical-radical reaction, is equal to the ratio k_d/k_r in the present paper. The values of k_d/k_c for vinyl radical reactions obtained by the previous and present workers are summarized in Table 5. The results of the present work and those of previous investigators are compatible except for the results of Sherwood and Gunning, although the vinyl radical sources and experimental conditions differ from each other.

Considering the results of photochemical study of Weir[4] and the present work, the value of the ratio k_d/k_c for vinyl radical seems to depend slightly on the exciting energy. When a molecule for free radical source is excited by absorption of quanta of shorter wavelength, the excess energy carried by the photofragment radical should be larger. The results in Table 5 suggest that the excitation by shorter wavelength light causes larger value of k_d/k_c in the case of vinyl radicals. It is difficult, however, to find a regularity from all the data in Table 5 taken from different studies since the conditions for vinyl radical formation differ.

It is generally accepted that recombination and disproportionation reactions of free radicals proceed with almost zero activation energy[14,15] as well as ion-molecule reactions.

It is also known that, in ion-molecule reactions, the "stripping" mechanism is predominant at high energy conditions whereas the "complex" mechanism is effective at low energy conditions.[16,17] In the reaction between CH_4^+ and CH_4, for example, H^+-stripping model was considered while the complex formation was assumed in low energy condition.[18]

$$\mathrm{CH_4^+ + CH_4}\begin{cases}\longrightarrow \mathrm{CH_3 + CH_5^+} & (\mathrm{H^+}\text{-stripping})\\ \longrightarrow \mathrm{C_2H_8^+} \longrightarrow \mathrm{CH_5^+ + CH_3} & (\text{complex})\end{cases}$$

It might be suggested that the observation of the complex(combination) → disproportionation transition with increasing exciting energy in radical-radical reactions is phenomenologically analogous to the complex → stripping transition with increasing energy found in ion-molecule reactions.

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