

# Reaction of Methyl Radical with Dimethyl Disulfide

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The reaction of dimethyl disulfide with methyl radical liberated by the photolysis of azomethane has been investigated at 100°C.

From the variation of the rates of formation of nitrogen, methane, ethane and thioether, a probable reaction scheme has been proposed, and on the basis of the assumed mechanism some relative values of the rate constants have been obtained.

## INTRODUCTION

It is well known that a variety of thiols<sup>1)</sup> and disulfides<sup>2)</sup> are utilized as modifiers or regulators in polymerization. The occurrence of chain transfer is, of course, due to the scission of S-H and S-S bonds by free radical attack, and this scission can be seen also in the other field of radical reactions.<sup>3)</sup> Since almost all of these investigations have been made in liquid phase, we have tried to test the possibility of the scission of S-H, S-S, C-S bonds in vapor phase. After some preliminary experiments a quantitative research has been made on the reaction of methyl radical with dimethyl disulfide which is the simplest substrate of S-S containing compounds.

At first, it seems to be significant to summarize briefly the results obtained in our preliminary studies. The reactions of H-atom formed by the photolysis of formaldehyde at 3130 Å with CH<sub>3</sub>SH, CH<sub>3</sub>SCH<sub>3</sub> and CH<sub>3</sub>SSCH<sub>3</sub> were investigated at 100°C (unpublished work). Quantitative data could not be obtained, but some features of the reaction were clarified from the product analyses.

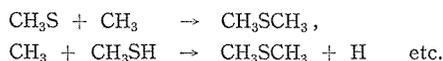
- (i) H and CH<sub>3</sub>SH: The hydrogen atom attached to S is quite easily abstracted and the liberated CH<sub>3</sub>S dimerizes to form disulfide. As H<sub>2</sub>S can not be detected, no scission of the bond C-S appears to occur.
- (ii) H and CH<sub>3</sub>SCH<sub>3</sub>: Although the hydrogen abstraction might take place, the scission of the bond C-S can not occur because CH<sub>3</sub>SH was not detected.
- (iii) H and CH<sub>3</sub>SSCH<sub>3</sub>: Since CH<sub>3</sub>SH was identified, the scission of the bond S-S may occur.

The reaction of methyl radical with CH<sub>3</sub>SH was tried under the same condition as in the case above using the photolysis of azomethane at 3650 Å. Again the hydrogen of the -SH group was abstracted easily and the liberated CH<sub>3</sub>S dimerized to form disulfide. Since no trace of H<sub>2</sub>, CH<sub>3</sub>SCH<sub>3</sub>, C<sub>2</sub>H<sub>6</sub> was detected,

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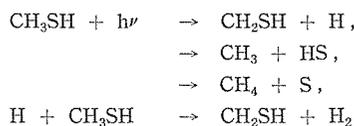
it seems that the hydrogen abstraction from the substrate by methyl radical is rapid and the reactions such as



can not take place. These findings are in accord with the conclusion of Inaba *et al.* in which they suggest the following mechanism on the photolysis of methyl mercaptan in vapor phase<sup>4)</sup>:



From the results using  $\text{CH}_3\text{SD}$  they found that other reactions, *e.g.*,



would not be important.

On the other hand, the quantum yield of disulfide decomposition in the photolysis of dimethyl disulfide investigated in our laboratory (unpublished work) was very low (0.01~0.001) and the detected products ( $\text{CH}_4$  and  $\text{CH}_3\text{SH}$ ) could not be main products. This low quantum yield would be explained if we consider that the reactivity of  $\text{CH}_3\text{S}$  radical is so low for the hydrogen abstraction that almost all of the radicals recombine to form disulfide again.

In the present investigation, the mechanism of the photolysis of azomethane alone is investigated at first. With this result the whole reaction mechanism in the reaction system of azomethane and dimethyl disulfide is studied to get the relative rate constants of the competitive elementary reactions.

## EXPERIMENTAL

Azomethane was prepared by the oxidation of dimethyl hydrazine hydrochloride (prepared from benzoyl chloride) with cupric chloride according to the method described by Jahn.<sup>5)</sup> The cuprous chloride addition complex was then decomposed at about 100°C and the azomethane liberated was dried over sodalime and calcium chloride and condensed at -76°C. After repetitions of bulb-to-bulb distillation the product was stored as vapor. Azomethane thus obtained was gaschromatographically pure.

Dimethyl disulfide was prepared by the method cited by Stevenson *et al.* through *Bunte* salt.<sup>6)</sup> After the purification by ether extraction and vacuum distillation, the compound stayed colorless for more than two months. The refractive index  $n_D^{20}$  observed was 1.5310, and no impurity was detected by gaschromatography. Disulfide was stored in liquid atate.

Methyl mercaptan and thioether were prepared by the usual method.<sup>7,8)</sup> These were also confirmed to be quite pure by gaschromatography.

## APPARATUS

A cylindrical glass reactor (41 mm. in diameter and 163 mm. long; volume 215 ml.) with a Telex-glass window at one open end, was placed in an electric furnace whose temperature was kept at  $100 \pm 1^\circ\text{C}$ .

On the other end the reactor had two capillary openings which were connected with the devices such as evacuation, reactant reservoirs, Toepler pump, manometer, and strain gauge membrane through silicone-greased cocks.

The pressure of azomethane in the reactor was measured indirectly with a strain meter. The membrane, on which a strain gauge is pasted, separates the reaction system from the pressure counterbalancing system. Then the deflection due to the pressure unbalance is counterbalanced by the air introduced into the balancing system to the zero point of strain meter, and the pressure in the balancing system is measured with the mercury manometer. In this way the contact of mercury and the reactant vapor was avoided.

## OPTICAL SYSTEM

A high pressure mercury lamp (SHLD-500 watt) was operated by D.C. 5.0 Amp. and the light beam collimated by a quartz lens was introduced into the reactor through the water cooled filters UVD2 (transparent in the region of 3200–3900 Å; transparency 3650 Å 69%, 3130 Å 21%), and the Telex window of the reactor (transparency 3650 Å 85%).

Referring to the intensity distribution of the lamp (approximate relative intensity: 4358 Å, 100; 4078 Å, 14; 3650 Å, 79; 3341 Å, 16; 3130 Å, 17; 3022 Å, 10; 2968 Å, 7; backgrounds, ca. 2) and the absorption of azomethane, the most effective wavelength introduced into the reactor must be 3650 Å (nearly monochromatic). The absorption curve of azomethane is reproduced in Fig. 1.<sup>11)</sup>

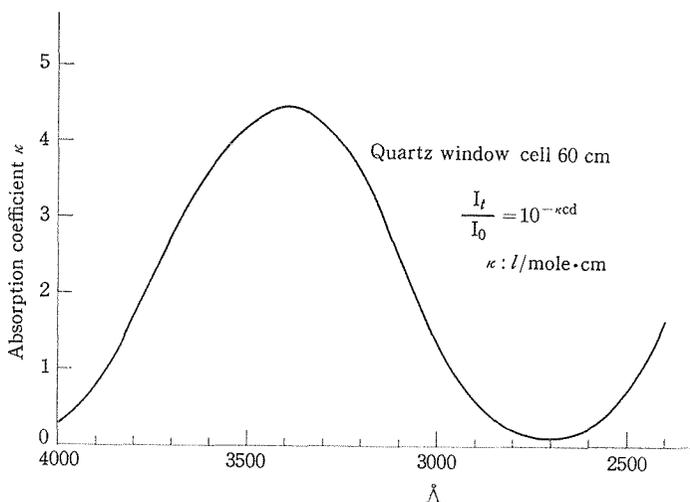


Fig. 1. Absorption curve of azomethane.<sup>11)</sup>

## ANALYSIS OF PRODUCTS

The materials from the reactor were transferred into the Toepler through a trap kept at  $-76^{\circ}\text{C}$  and separated into uncondensable gas and liquid. Both of them were analyzed by gaschromatography, the conditions being as follows:

For  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ; Alumina 4 m.,  $\text{H}_2(\text{N}_2)$ ,  $31^{\circ}\text{C}$ .

For azomethane; Tricresyl phosphate 4 m.,  $\text{H}_2$ ,  $30^{\circ}\text{C}$ .

For thioether, ethanol, disulfide; Tricresyl phosphate 4 m.,  $\text{H}_2$ ,  $87^{\circ}\text{C}$ .

## RESULTS

(A) The photolysis of azomethane

No thermal dark reaction was observed at  $100^{\circ}\text{C}$ .

The initial pressure of azomethane was varied from 10 to 60 mm., and the ranges of conversions were 0–60%.

Results of the product analyses are given in Table 1. The products detected are nitrogen, methane, and ethane. The ratios  $(\text{CH}_4 + 2\text{C}_2\text{H}_6)/\text{N}_2$  are less than 2 (nearly 1.4–1.6). Hydrogen, ethylene, propane, propylene, hydrogen sulfide and methyl mercaptan were not detected.

Table 1. The photolysis of azomethane.

Run no.	Irradiation time (t) min.	Initial amount of azomethane ( $A_0$ ) millimole	Fraction of remaining azomethane ( $\gamma$ )	Products millimole		
				$\text{N}_2$	$\text{CH}_4$	$\text{C}_2\text{H}_6$
G-8	0	0.275	0.986	trace	0	0
G-10	2	.231	.853	—	—	—
G-11	3	.222	.865	0.0106	0.00074	0.00125
G-9	5	.231	.918	.0149	.00337	.00965
G-6	10	.307	.792	.0252	.00788	.0126
G-3	20	.356	.747	.0534	.0115	.0222
G-5	30	.328	.720	.0570	.0189	.0325
G-2	40	.369	.620	.1054	.0262	.0479
G-1	60	.333	.624	.1472	.0259	.0478
G-7	70	.295	.540	.1000	.0307	.0623
D-6	90	.194	.660	.0915	.0174	.0318
D-4	90	.307	.472	.1086	.0309	.0617
D-5	90	.497	.537	.1810	.0492	.1070
G-4	120	.385	.385	.1490	.0446	.0915

(B) The photolysis of the mixture of azomethane and dimethyl disulfide.

The ranges of initial pressure of azomethane and disulfide were 10–50 mm. and 5–100 mm., respectively, *i.e.* the molar ratios of the reactants were from 0.1 to 0.8.

Results of the product analyses are given in Table 2.

In this case, thioether (TE) was identified in liquid product. The ratios  $\frac{\text{CH}_4 + 2\text{C}_2\text{H}_6}{\text{N}_2}$  are fairly low, but  $\frac{\text{CH}_4 + 2\text{C}_2\text{H}_6 + \text{TE}}{\text{N}_2}$  are again 1.4–1.6.

## Reaction of Methyl Radical with Dimethyl Disulfide

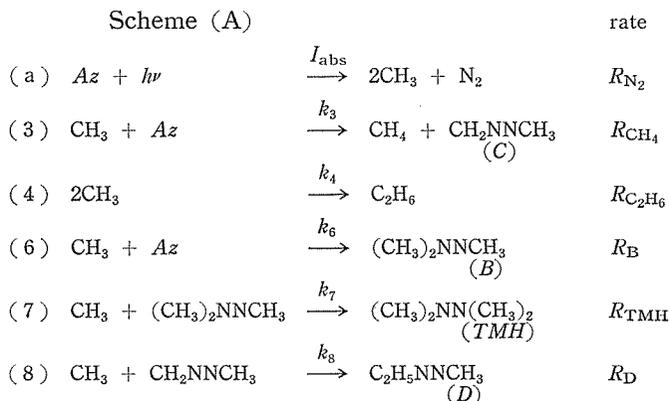
Table 2. The photolysis in the system of azomethane and dimethyl disulfide.

Run No.	Irradiation time ( $t$ ) min.	Initial amount of azomethane ( $A_0$ ) millimole	Fraction of remaining azomethane ( $\gamma$ )	Initial amount of disulfide ( $DS_0$ ) millimole	Products millimole			
					N <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> SCH <sub>3</sub>
F-2	30	0.269	0.816	0.196	0.0440	0.0192	0.0155	0.0142
F-1	62	.357	.521	.213	.1156	.0503	.0346	.0540
E-1	91	.320	.443	.220	.1514	.0589	.0420	.0797
E-2	92	.302	.358	.222	.129	.0500	.0317	.0690
F-3	120	.345	.255	.211	.164	.0623	.0342	.0674
F-4	125	.308	.438	.203	.130	.0656	.0374	.0775
E-4	90	.240	.500	.745	.116	.0537	.0098	.1036
E-5	90	.132	.415	.872	.0643	.0413	.0021	.0532
E-6	90	.430	.377	.056	.164	.0647	.0840	.0167
E-7	90	.234	.520	.362	.103	.0438	.0238	.077
E-8	90	.122	.446	.405	.0528	.0200	.0067	.0424
E-9	90	.117	.436	.989	.0396	.0241	.0004	.0376

## Reaction Mechanism and Relative Rate Constants

(A) The system of azomethane alone

After some trials, we have reached the following reaction mechanism analogous to that proposed by Jones and Steacie<sup>9)</sup>.



Although the presence of the products of reactions (7) and (8) could not be proved, we assumed them to account for the disappearance of the radicals  $B$  and  $C$ . The formation of tetramethyl-hydrazine and methyl-ethyl-diimide have been suggested by Steacie *et al.* from the results of mass-spectrography.<sup>6)</sup>

From this scheme, we have

$$\frac{dM}{dt} = 2I_{\text{abs}} - R_{\text{CH}_4} - 2R_{\text{C}_2\text{H}_6} - R_B - R_{\text{TMH}} - R_D, \quad (1)$$

where

$$M \equiv [\text{CH}_3], \quad B \equiv [(\text{CH}_3)_2\text{NNCH}_3], \quad C \equiv [\text{CH}_2\text{NNCH}_3], \\ D \equiv [\text{CH}_3\text{NNC}_2\text{H}_5], \quad \text{TMH} \equiv [(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2], \quad \text{respectively.}$$

If almost all of the radicals  $B$  and  $C$  are stabilized by reaction (7) and (8), the fraction of azomethane decomposition,  $\beta$ , can be given by

$$\beta = 1 - \frac{A_t}{A_0} = \frac{1}{A_0} (2[\text{N}_2] - [\text{C}_2\text{H}_6]), \quad A \equiv [\text{CH}_3\text{N}_2\text{CH}_3],$$

in which the suffix 0 denotes the initial state.

Fig. 2 shows a good agreement of this value with the observation.

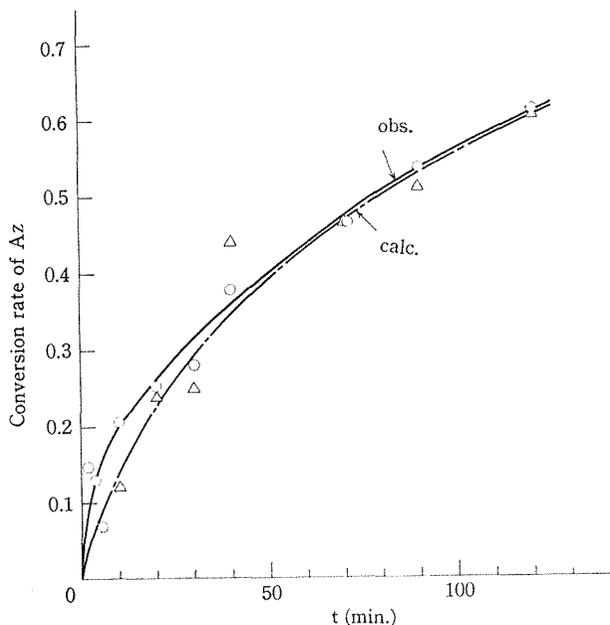


Fig. 2. Comparison of  $\beta_{\text{obs}}$  with  $\beta_{\text{calc}}$  in the scheme A.

Based on the mechanism assumed here we can estimate the value of the relative rate constant  $k_3/k_4^{1/2}$ .

From equation (1) we have

$$k_4 M^2 + 2(k_3 + k_6)A \cdot M - 2I_{\text{abs}} = 0. \quad (2)$$

By approximation\*<sup>2)</sup> this equation can be solved as  $M \doteq \sqrt{\frac{K}{k_4}} A^{1/2}$  ( $K$ ; constant in the present investigation) and the amounts of each product are given by the following equations:

$$\begin{aligned} [\text{CH}_4] &= \sqrt{K} \cdot \frac{k_3}{k_4^{1/2}} A_0^{3/2} \int_0^t \gamma^{3/2} dt, \\ [\text{C}_2\text{H}_6] &= K A_0 \int_0^t \gamma dt, \end{aligned}$$

\* Two approximations are used:

- (1) In the solution of eq. (2),  $M = \frac{-(k_3 + k_6)A + \sqrt{(k_3 + k_6)^2 A^2 + 2k_4 I_{\text{abs}}}}{k_4}$ , the first term in the root sign is very small as compared with the second. This was shown by numerical calculation using observed data.
- (2) Only the first power term in the expansion of  $I_{\text{abs}}$  with  $A$ , is taken into account.

Thus,  $M \doteq \sqrt{\frac{2I_{\text{abs}}}{k_4}} \doteq \sqrt{\frac{KA}{k_4}}$ ,  $K$  being a constant throughout the experiment.

where  $\gamma$  is the ratio of remaining azomethane, therefore

$$\frac{[\text{CH}_4]}{[\text{C}_2\text{H}_6]^{\frac{1}{2}}} = \frac{k_3}{k_4^{\frac{1}{2}}} \times f \cdot A_0,$$

$$f = \frac{\int_0^t \gamma^{\frac{3}{2}} dt}{\left\{ \int_0^t \gamma dt \right\}^{\frac{1}{2}}}. \quad (3)$$

Then the value  $k_3/k_4^{\frac{1}{2}}$  can be estimated from the relationship (3) by plotting  $\text{CH}_4/\text{C}_2\text{H}_6^{\frac{1}{2}}$  against  $f \cdot A_0$ . ( $f$  can be estimated from the observed curve of azomethane decomposition by graphical integration.) As is seen in Fig. 3, we get

$$\frac{k_3}{k_4^{\frac{1}{2}}} = 0.0655 \times V^{\frac{1}{2}} \frac{l^{\frac{1}{2}}}{\text{mM}^{\frac{1}{2}} \cdot \text{min}^{-\frac{1}{2}}},$$

$V$ : reactor volume, 215 ml, here.

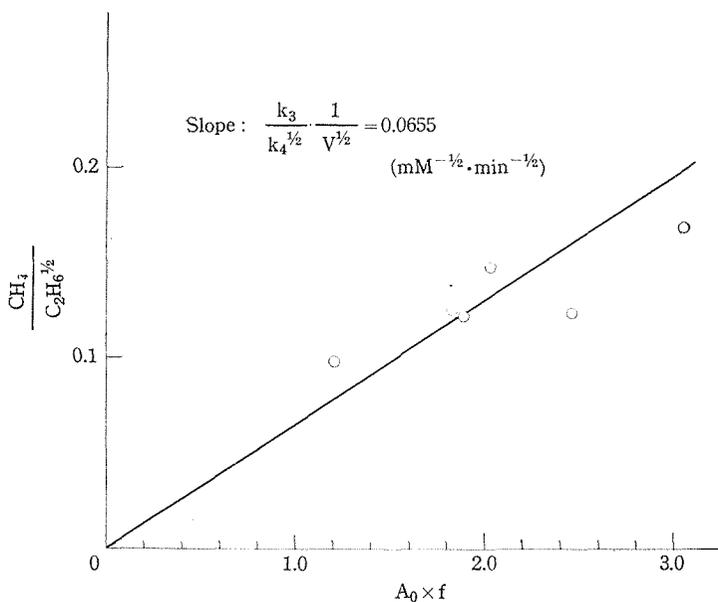


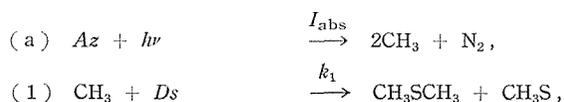
Fig. 3. Linear relationship in eq. 3.

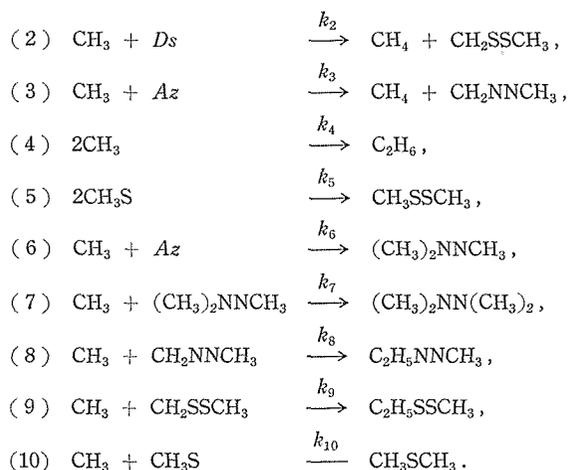
(B) The system of azomethane and disulfide.

Considering the observed facts given below, we propose the following reaction mechanism for the azomethane and disulfide system, in which the scheme (A) given before is involved.

- i) Thiyl radical  $\text{CH}_3\text{S}$  dimerized to form  $\text{CH}_3\text{SSCH}_3$ .
- ii)  $\text{CH}_3\text{SH}$  and  $\text{H}_2\text{S}$  could not be detected but thioether was identified.

Scheme (B).





By the similar treatment as before, we have

$$\beta = 1 - \frac{A_t}{A_0} = \frac{1}{A_0} \left( 2[\text{N}_2] - [\text{C}_2\text{H}_6] - \frac{1}{2} [TE] \right).$$

Fig. 4 shows the calculated value and observed  $\beta_{\text{obs}}$ .

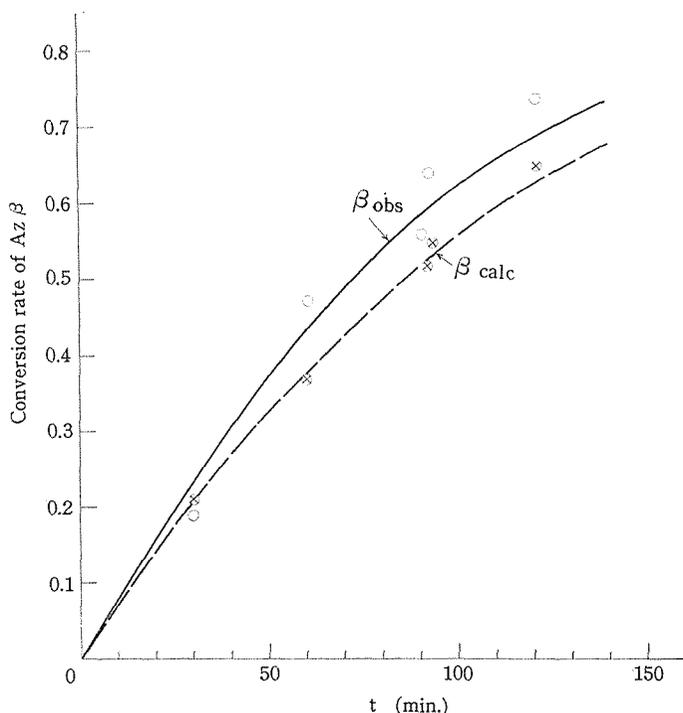


Fig. 4. Comparison of  $\beta_{\text{obs}}$  with  $\beta_{\text{calc}}$  in the scheme B.

The difference may be considered to be within experimental errors.

In this system, the concentration of methyl radical can be expressed by the equation,

$$k_4 M^2 + \{(k_1 D_s + k_{10} T) + 2(k_2 D_s + k_3 A) + 2k_6 A\} M - 2I_{\text{abs}} = 0. \quad (4)$$

By the similar approximation as in the case (A), the equation can be solved as

$$M = \sqrt{\frac{K}{k_4}} \cdot A^{\frac{1}{2}}.$$

Then,

$$[\text{CH}_4] = \frac{k_2}{k_4^{\frac{1}{2}}} \cdot K^{\frac{1}{2}} D_{s_0} \cdot A_0^{\frac{1}{2}} \int_0^t \gamma^{\frac{1}{2}} dt + \frac{k_3}{k_4^{\frac{1}{2}}} \cdot K^{\frac{1}{2}} \cdot A_0^{\frac{3}{2}} \int_0^t \gamma^{\frac{3}{2}} dt, \quad (5)$$

$$[\text{C}_2\text{H}_6] = K \cdot A_0 \int_0^t \gamma dt, \quad (6)$$

$$[\text{TE}] = \frac{k_1 - k_2}{k_4^{\frac{1}{2}}} K^{\frac{1}{2}} \cdot A_0^{\frac{1}{2}} D_{s_0} \int_0^t \gamma^{\frac{1}{2}} dt, \quad (7)$$

hence,

$$\frac{[\text{CH}_4]}{[\text{C}_2\text{H}_6]^{\frac{1}{2}}} = \frac{k_2}{k_4^{\frac{1}{2}}} \times D_{s_0} \cdot f_{\text{I}} + \frac{k_3}{k_4^{\frac{1}{2}}} \times A_0 \cdot f_{\text{II}}, \quad (8)$$

where

$$f_{\text{I}} = \frac{\int_0^t \gamma^{\frac{1}{2}} dt}{\left\{ \int_0^t \gamma dt \right\}^{\frac{1}{2}}}, \quad f_{\text{II}} = \frac{\int_0^t \gamma^{\frac{3}{2}} dt}{\left\{ \int_0^t \gamma dt \right\}^{\frac{1}{2}}}.$$

Thus  $k_2/k_4^{\frac{1}{2}}$  can be obtained from the relation (8) by plotting  $\frac{[\text{CH}_4]}{[\text{C}_2\text{H}_6]^{\frac{1}{2}}} - \frac{k_3}{k_4^{\frac{1}{2}}} \cdot A_0 f_{\text{II}}$  against  $D_{s_0} f_{\text{I}}$ , in which  $k_3/k_4^{\frac{1}{2}}$  is already known in the case (A). ( $k_3/k_4^{\frac{1}{2}} = 0.0655 \times V^{\frac{1}{2}}, 1.1^{\frac{1}{2}} \text{ mM}^{-\frac{1}{2}} \text{ min}^{-\frac{1}{2}}$ ) Fig. 5 gives  $k_2/k_4^{\frac{1}{2}} = 0.0617 \times V^{\frac{1}{2}} \text{ l}^{\frac{1}{2}} \text{ m}^{-\frac{1}{2}}, \text{ min}^{-\frac{1}{2}}$  and combining this with  $k_3/k_4^{\frac{1}{2}}$  we have  $k_2/k_3 = 0.94$ .

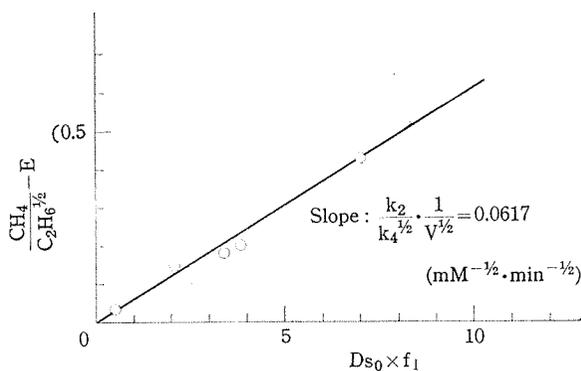


Fig. 5. Linear relationship in eq. 8.

Meanwhile the ratio  $k_2/k_3$  is also given by the equation (5) and (7), that is,

$$\frac{[\text{CH}_4]}{[\text{TE}]} = \frac{k_2}{k_1 - k_2} + \frac{k_3}{k_1 - k_2} \frac{A_0}{D_{s_0}} \cdot f_{\text{III}}, \quad (9)$$

where  $f_{\text{III}} = \frac{\int_0^t \gamma^{\frac{3}{2}} dt}{\int_0^t \gamma^{\frac{1}{2}} dt}$ .

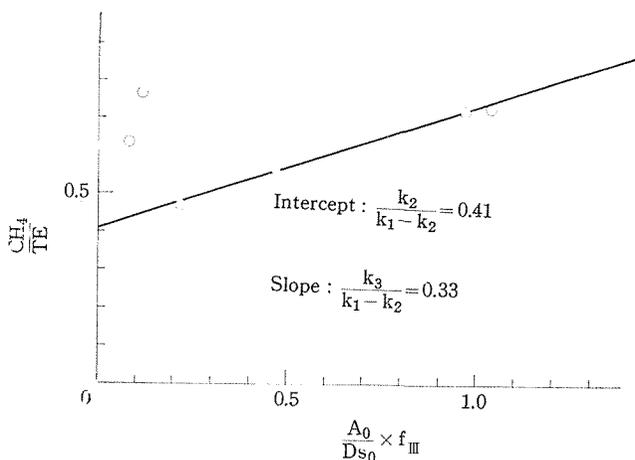


Fig. 6. Linear relationship in eq. 9.

From (9) (Fig. 6) we have  $k_2/k_3=1.25$  and accordingly  $k_1/k_2=3.44$ .

Applying the similar treatment to the equations (6) and (7), the ratio  $k_1/k_2$  is also obtained:

$$\frac{[TE]}{[C_2H_6]^{\frac{1}{2}}} = \frac{k_1 - k_2}{k_4^{\frac{1}{2}}} \cdot Ds_0 \cdot f_I \quad (10)$$

Fig. 7 gives  $\frac{k_1 - k_2}{k_4^{\frac{1}{2}}} = 0.150 \times V^{\frac{1}{2}}$  ( $1.5^{\frac{1}{2}} \text{ mM}^{-\frac{1}{2}} \text{ min.}^{-\frac{1}{2}}$ ). Since  $k_2/k_4^{\frac{1}{2}} = 0.0617$ , we have  $k_1/k_4^{\frac{1}{2}} = 0.212 \times V^{\frac{1}{2}}$  ( $1.5^{\frac{1}{2}} \text{ mM}^{-\frac{1}{2}} \text{ min.}^{-\frac{1}{2}}$ ) the ratio  $k_1/k_2$  becomes 3.44.

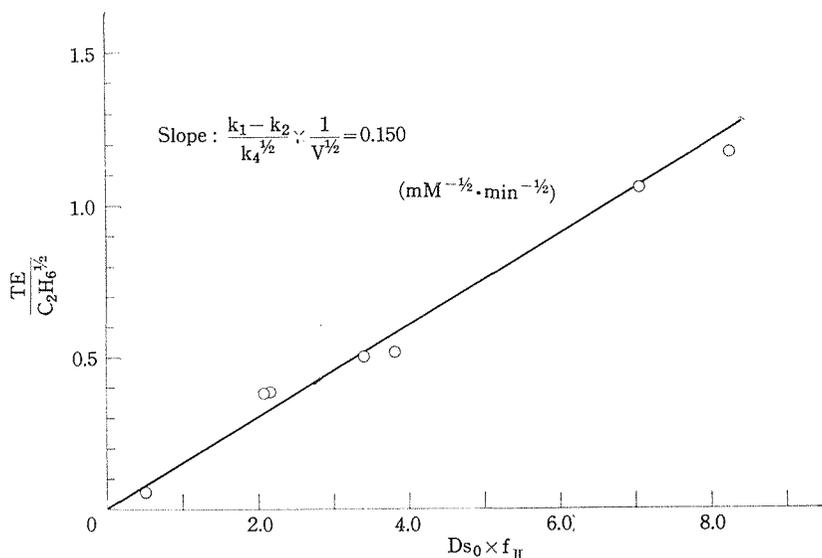


Fig. 7. Linear relationship derived from eq. 10.

The two values of each  $k_2/k_3$  and  $k_1/k_2$  obtained above seem to coincide fairly well and this would support the proposed scheme (B).

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Here, when the absolute value of  $k_4$  is taken as  $2 \times 10^{13} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ . ( $1.2 \times 10^9 \text{ l. mM}^{-1} \cdot \text{min}^{-1}$ ) from the published papers<sup>10)</sup>, the relative ratio  $k_1/k_4$  becomes  $3 \times 10^{-6}$  at  $100^\circ\text{C}$ .

### CONCLUSION

In the system of methyl radical and dimethyl disulfide, the formation of thioether shows the scission S-S bond. Referring to the qualitative results on the system of H-atom and sulfur compounds and of methyl radical and methyl mercaptan, a probable scheme (B) has been suggested. Based on this scheme, the relative values of the rate constants at  $100^\circ\text{C}$  have been estimated:

$$\begin{aligned}\frac{k_1}{k_4} &= \frac{k(\text{S-S scission by } \text{CH}_3)}{k(\text{recombination of } \text{CH}_3)} \simeq 3 \times 10^{-6}, \\ \frac{k_2}{k_3} &= \frac{k(\text{H-abstraction from disulfide})}{k(\text{H-abstraction from azomethane})} \simeq 1, \\ \frac{k_1}{k_2} &= \frac{k(\text{S-S scission by } \text{CH}_3)}{k(\text{H-abstraction by } \text{CH}_3 \text{ from disulfide})} \simeq 3.4.\end{aligned}$$

Since the number of hydrogen and sulfur atoms in the substrate is 6 and 2 respectively, the relative reactivity of one H atom in C-H bond and one S atom in S-S bond becomes 1:10 (at  $100^\circ\text{C}$ ) towards methyl attack.

### REFERENCES

- (1) C. Walling, *J. Am. Chem. Soc.*, **70**, 2561 (1948); W. V. Smith, *ibid.*, **68**, 2059 (1946); R. A. Gregg, D. M. Alderman, and F. R. Mayo, *ibid.*, **70**, 3740 (1948); E. J. Meehan, I. M. Kolthoff, and P. R. Sinha, *J. Polymer Sci.*, **16**, 471 (1955); R. M. Pierson, A. J. Costanza, and A. H. Weinstein, *ibid.*, **17**, 221 (1955).
- (2) A. V. Tobolsky and B. Baysal, *J. Am. Chem. Soc.*, **75**, 1757 (1953).
- (3) M. Onyszchuk, *Can. J. Chem.*, **33**, 1034 (1955); C. Sivertz, W. Andreus, W. Elsdon, and K. Graham, *J. Polymer Sci.*, **19**, 587 (1956); W. E. Lyons, *Nature*, **162**, 1004 (1948).
- (4) T. Inaba and B. deB. Darwent, *J. Phys. Chem.*, **64**, 1431 (1960).
- (5) F. P. Jahn, *J. Am. Chem. Soc.*, **59**, 1761 (1937).
- (6) D. P. Stevenson and J. Y. Beach, *ibid.*, **60**, 2874 (1938).
- (7)  $\text{CH}_3\text{SH}$ ; L. Vanino "Präparative Chemie" p. 88, Ferdinand Enke, Stuttgart (1937).
- (8)  $\text{CH}_3\text{SCH}_3$ ; Romeo B. Wagner "Synthetic Organic Chemistry" p. 787, Wiley, New York, (1953).
- (9) M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953).
- (10) *e.g.*, R. Gomer and G. B. Kistiakowsky, *ibid.*, **19**, 85 (1951); G. B. Kistiakowsky and E. K. Roberts, *ibid.*, **21**, 1637 (1953); A. Shepp, *ibid.*, **24**, 939 (1956) *etc.*
- (11) H. C. Ramsperger, *J. Am. Chem. Soc.*, **50**, 123 (1928).