KURENAI

Kyoto University Research Information Repository

KYOTO UNIVERSITY

Title	Reaction of Methyl Radical with Dimethyl Disulfide
Author(s)	Suama, Masakazu; Takezaki, Yoshimasa
Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1962), 40(4): 229-239
Issue Date	1962-09-20
URL	http://hdl.handle.net/2433/75899
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Kyoto University

Reaction of Methyl Radical with Dimethyl Disulfide

Masakazu Suama and Yoshimasa Takezaki*

(Takezaki Laboratory)

   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[1] and disulfides[2] 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.[3] 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formed by the photolysis of formaldehyde at 3130 Å with CH_3SH, CH_3SCH_3 and CH_3SSCH_3 were investigated at 100°C (unpublished work).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_3SH: The hydrogen atom attached to S is quite easily abstracted and the liberated CH_3S dimerizes to form disulfide. As H_2S can not be detected, no scission of the bond C–S appears to occur.

   (ii) H and CH_3SCH_3: Although the hydrogen abstraction might take place, the scission of the bond C–S can not occur because CH_3SH was not detected.

   (iii) H and CH_3SSCH_3: Since CH_3SH was identified, the scission of the bond S–S may occur.

The reaction of methyl radical with CH_3SH 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_3S dimerized to form disulfide. Since no trace of H_2, CH_3SCH_3, C_2H_6 was detected,

---

* 須天正和, 竹崎嘉真

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

$$CH_3S + CH_3 \rightarrow CH_3SCH_3,$$
$$CH_3 + CH_3SH \rightarrow CH_3SCH_3 + H \quad \text{etc.}$$
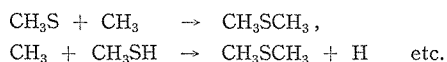
can not take place. These findings are in accord with the conclusion of Inaba *et al.* in which they suggest the following mechanism on the photolysis of methyl mercaptan in vapor phase[4] :

$$CH_3SH + h\nu \rightarrow CH_3S + H,$$
$$H + CH_3SH \rightarrow CH_3S + H_2,$$
$$2CH_3S \rightarrow CH_3SSCH_3.$$
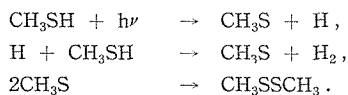
From the results using CH_3SD they found that other reactions, *e.g.*,

$$CH_3SH + h\nu \rightarrow CH_2SH + H,$$
$$\rightarrow CH_3 + HS,$$
$$\rightarrow CH_4 + S,$$
$$H + CH_3SH \rightarrow CH_2SH + H_2$$
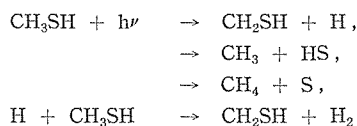
would not be important.

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 ($0.01 \sim 0.001$) and the detected products (CH_4 and CH_3SH) could not be main products. This low quantum yield would be explained if we consider that that the reactivity of CH_3S 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 hydro-chloride (prepared from benzoyl chloride) with cupric chloride according to the methode described by Jahn.[5] 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.[6] After the purification by ether extraction and vacuum distillation, the compound stayed colorless for more than two months. The refractive index n_D^{16} observed was 1.5310, and no impurity was detected by gas-chromatography. Disulfide was stored in liquid atate.

Methyl mercaptan and thioether were prepared by the usual method.[7,8] 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 $100\pm1°$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.[11]
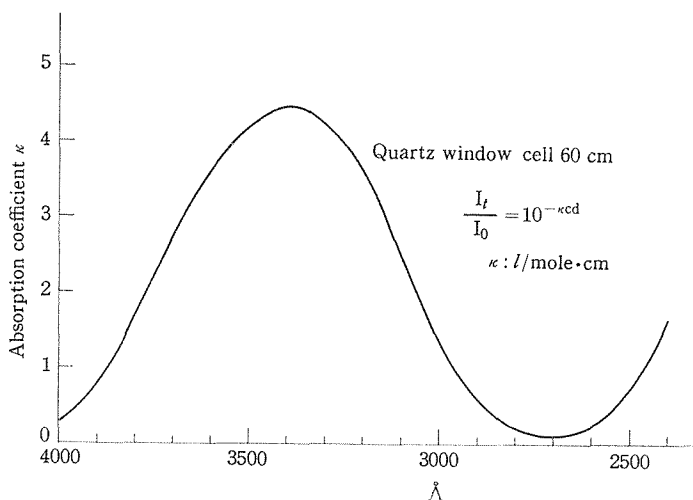

Fig. 1. Absorption curve of azomethane.[11]

ANALYSIS OF PRODUCTS

The materials from the reactor were transfered into the Toepler through a trap kept at $-76°C$ and seperated into uncondensable gas and liquid. Both of them were analyzed by gaschromatography, the conditions being as follows:

For N_2, CH_4, C_2H_6; Alumina 4 m., $H_2(N_2)$, 31°C.

For azomethane; Tricresyl phosphate 4 m., H_2, 30°C.

For thioether, ethanol, disulfide; Tricresyl phosphate 4 m., H_2, 87°C.

RESULTS

(A) The photolysis of azomethane

No thermal dark reaction was observed at 100°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 $(CH_4+2C_2H_6)/N_2$ 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 (γ)	Products millimole		
				N_2	CH_4	C_2H_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 $\dfrac{CH_4+2C_2H_6}{N_2}$ are fairly low, but $\dfrac{CH_4+2C_2H_6+TE}{N_2}$ are again 1.4—1.6.
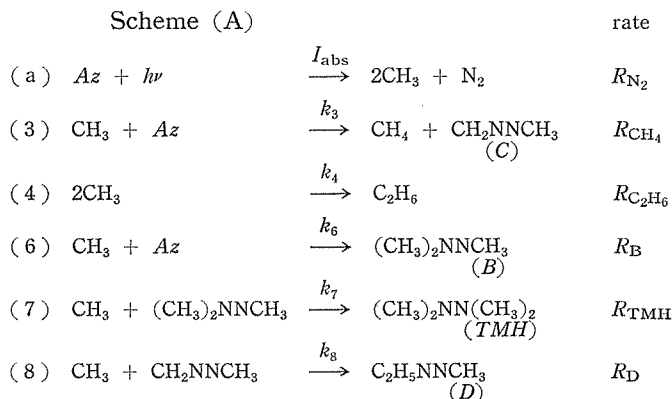
Table 2. The photolysis in the system of azomethane and dimethyl disulfide.

Run No.	Irradiation time (t) min.	Initial amount of azomethane (A_0) millimole	Fraction of remaining azomethane (γ)	Initial amount of disulfide (Ds_0) millimole	Products millimole			
					N_2	CH_4	C_2H_6	CH_3SCH_3
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[9].

Scheme (A)   rate

(a) $Az + h\nu \xrightarrow{I_{abs}} 2CH_3 + N_2$ $\qquad R_{N_2}$

(3) $CH_3 + Az \xrightarrow{k_3} CH_4 + \underset{(C)}{CH_2NNCH_3}$ $\qquad R_{CH_4}$

(4) $2CH_3 \xrightarrow{k_4} C_2H_6$ $\qquad R_{C_2H_6}$

(6) $CH_3 + Az \xrightarrow{k_6} \underset{(B)}{(CH_3)_2NNCH_3}$ $\qquad R_B$

(7) $CH_3 + (CH_3)_2NNCH_3 \xrightarrow{k_7} \underset{(TMH)}{(CH_3)_2NN(CH_3)_2}$ $\qquad R_{TMH}$

(8) $CH_3 + CH_2NNCH_3 \xrightarrow{k_8} \underset{(D)}{C_2H_5NNCH_3}$ $\qquad R_D$

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.[6]

From this scheme, we have

$$\frac{dM}{dt} = 2I_{abs} - R_{CH_4} - 2R_{C_2H_6} - R_B - R_{TMH} - R_D , \qquad (1)$$

where

$M \equiv [CH_3], \quad B \equiv [(CH_3)_2NNCH_3], \quad C \equiv [CH_2NNCH_3],$

$D \equiv [CH_3NNC_2H_5], \quad TMH \equiv [(CH_3)_2NN(CH_3)_2], \quad$ respectively.

(233)

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

$$\beta = 1-\frac{A_t}{A_0} = \frac{1}{A_0}(2[N_2]-[C_2H_6]) , \quad A \equiv [CH_3N_2CH_3] ,$$

in wich the suffix 0 denotes the initial state.

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

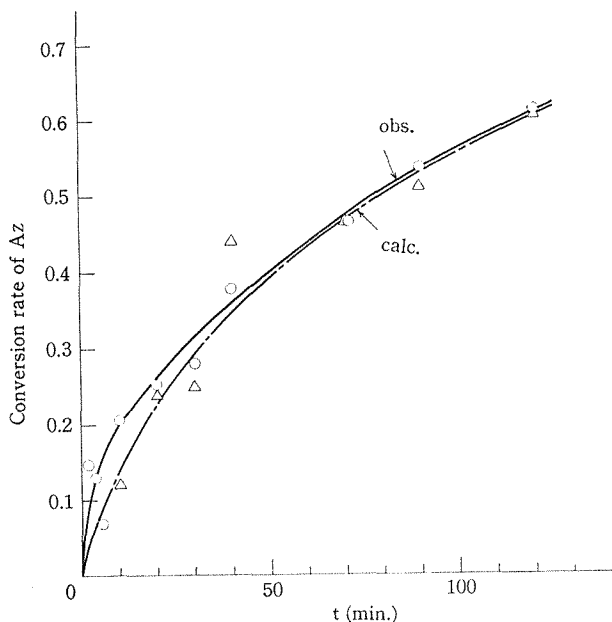Fig. 2. Comparison of β_{obs} with β_{calc} in the scheme A.

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

From equation (1) we have

$$k_4M^2+2(k_3+k_6)A \cdot M-2I_{abs} = 0 . \tag{2}$$

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

$$[CH_4] = \sqrt{K} \cdot \frac{k_3}{k_4^{\frac{1}{2}}} A_0^{\frac{3}{2}} \int_0^t \dot{r}^{\frac{1}{2}} dt ,$$

$$[C_2H_6] = KA_0 \int_0^t \dot{r} dt ,$$

---

* Two approximations are used:

(1) In the solution of eq. (2), $M = \dfrac{-(k_3+k_6)A+\sqrt{(k_3+k_6)_2A_2+2k_4I_{abs}}}{k_4}$, 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_{abs} with A, is taken into account.

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

where γ is the ratio of remaining azomethane, therefore

$$\frac{[CH_4]}{[C_2H_6]^{\frac{1}{2}}} = \frac{k_3}{k_4^{\frac{1}{2}}} \times f \cdot A_0 ,$$

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

Then the value $k_3/k_4^{\frac{1}{2}}$ can be estimated from the relationship (3) by plotting $CH_4/C_2H_6^{\frac{1}{2}}$ 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

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

V: reactor volume, 215 ml, here.

Slope: $\dfrac{k_3}{k_4^{1/2}} \cdot \dfrac{1}{V^{1/2}} = 0.0655$ $(mM^{-1/2} \cdot \min^{-1/2})$
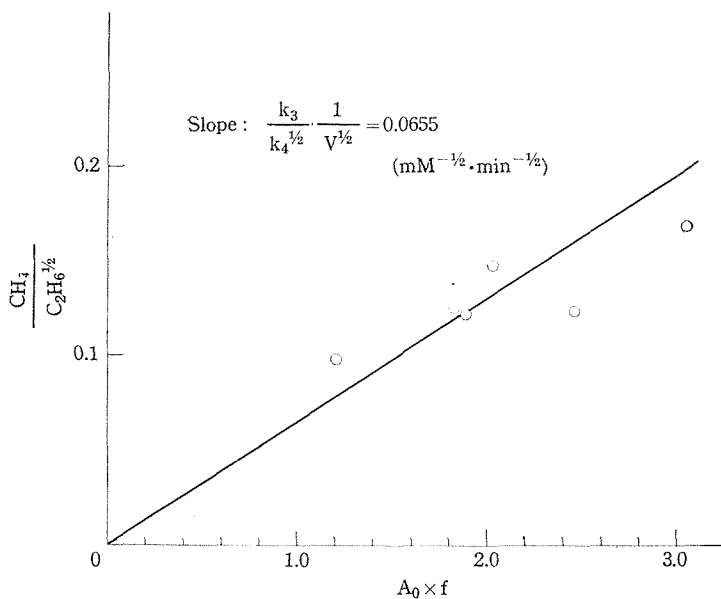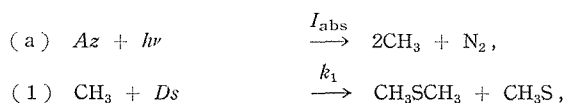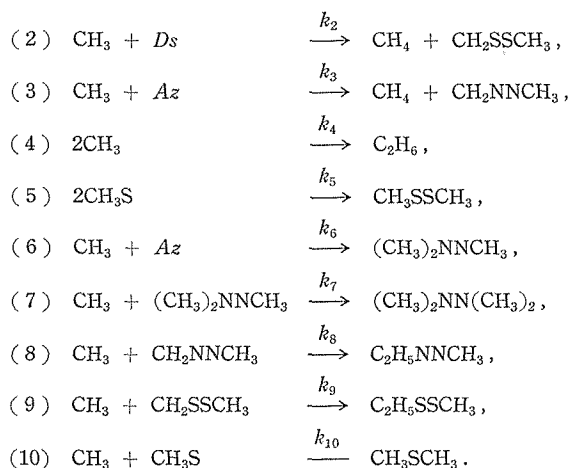
Fig. 3. Linear relationship in eq. 3.

(B) The system of azomethane and disulfide.

Considering the observed facts gived 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 CH_3S dimerized to form CH_3SSCH_3.

ii) CH_3SH and H_2S could not be detected but thioether was indentified.

Scheme (B).

(a) $Az + h\nu \xrightarrow{I_{abs}} 2CH_3 + N_2$,

(1) $CH_3 + Ds \xrightarrow{k_1} CH_3SCH_3 + CH_3S$,

$$(2)\quad CH_3 + Ds \xrightarrow{k_2} CH_4 + CH_2SSCH_3 ,$$

$$(3)\quad CH_3 + Az \xrightarrow{k_3} CH_4 + CH_2NNCH_3 ,$$

$$(4)\quad 2CH_3 \xrightarrow{k_4} C_2H_6 ,$$

$$(5)\quad 2CH_3S \xrightarrow{k_5} CH_3SSCH_3 ,$$

$$(6)\quad CH_3 + Az \xrightarrow{k_6} (CH_3)_2NNCH_3 ,$$

$$(7)\quad CH_3 + (CH_3)_2NNCH_3 \xrightarrow{k_7} (CH_3)_2NN(CH_3)_2 ,$$

$$(8)\quad CH_3 + CH_2NNCH_3 \xrightarrow{k_8} C_2H_5NNCH_3 ,$$

$$(9)\quad CH_3 + CH_2SSCH_3 \xrightarrow{k_9} C_2H_5SSCH_3 ,$$

$$(10)\quad CH_3 + CH_3S \xrightarrow{k_{10}} CH_3SCH_3 .$$

By the similar treatment as before, we have

$$\beta = 1 - \frac{A_t}{A_0} = \frac{1}{A_0}\left(2[N_2] - [C_2H_6] - \frac{1}{2}[TE] \right).$$

Fig. 4 shows the calculated value and observed β_{obs}.
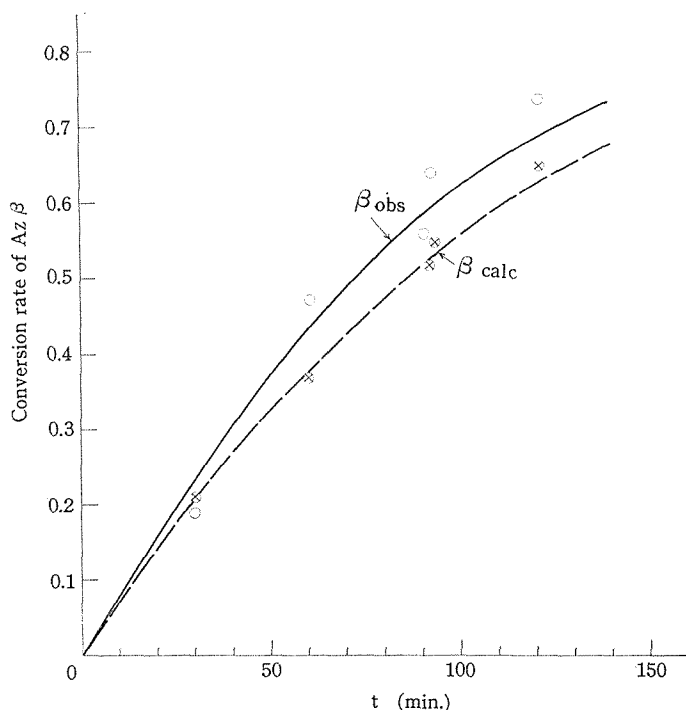
Fig. 4. Comparison of β_{obs} with β_{calc} in the scheme B.

The difference may be considered to be within experimental errors.

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

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

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

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

Then,

$$[CH_4] = \frac{k_2}{k_4^{\frac{1}{2}}} \cdot K^{\frac{1}{2}} Ds_0 \cdot A_0^{\frac{1}{2}} \int_0^t \gamma^{\frac{1}{2}} dt + \frac{k_3}{k_4^{\frac{1}{2}}} \cdot K^{\frac{1}{2}} \cdot A_0^{\frac{3}{2}} \int_0^t \gamma^{\frac{1}{2}} dt , \tag{5}$$

$$[C_2 H_6] = K \cdot A_0 \int_0^t \gamma dt , \tag{6}$$

$$[TE] = \frac{k_1 - k_2}{k_4^{\frac{1}{2}}} K^{\frac{1}{2}} \cdot A_0^{\frac{1}{2}} Ds_0 \int_0^t \gamma^{\frac{1}{2}} dt , \tag{7}$$

hence,

$$\frac{[CH_4]}{[C_2 H_6]^{\frac{1}{2}}} = \frac{k_2}{k_4^{\frac{1}{2}}} \times Ds_0 \cdot f_I + \frac{k_3}{k_4^{\frac{1}{2}}} \times A_0 \cdot f_{II} , \tag{8}$$

where

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

Thus $k_2/k_4^{\frac{1}{2}}$ can be obtained from the relation (8) by plotting $\frac{[CH_4]}{[C_2 H_6]^{\frac{1}{2}}} - \frac{k_3}{k_4^{\frac{1}{2}}} \cdot A_0 f_{II}$ against $Ds_0 f_I$, in which $k_3/k_4^{\frac{1}{2}}$ is already known in the case (A). ($(k_3/k_4^{\frac{1}{2}} = 0.0655 \times V^{\frac{1}{2}}, 1.^{\frac{1}{2}} \ mM^{-\frac{1}{2}} \ min.^{-\frac{1}{2}})$ Fig. 5 gives $k_3/k_4^{\frac{1}{2}} = 0.0617 \times V^{\frac{1}{2}} \ l^{\frac{1}{2}} m \ M^{-\frac{1}{2}}, \ min.^{-\frac{1}{2}}$ and combining this with $k_3/k_4^{\frac{1}{2}}$ we have $k_2/k_3 = 0.94$.
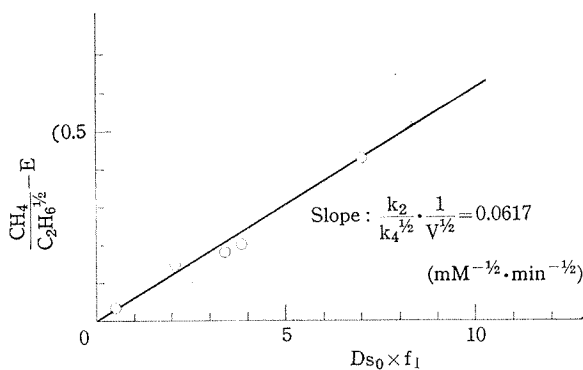

Fig. 5. Liner relationship in eq. 8.

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

$$\frac{[CH_4]}{[TE]} = \frac{k_2}{k_1 - k_2} + \frac{k_3}{k_1 - k_2} \frac{A_0}{Ds_0} \cdot f_{III} , \tag{9}$$

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

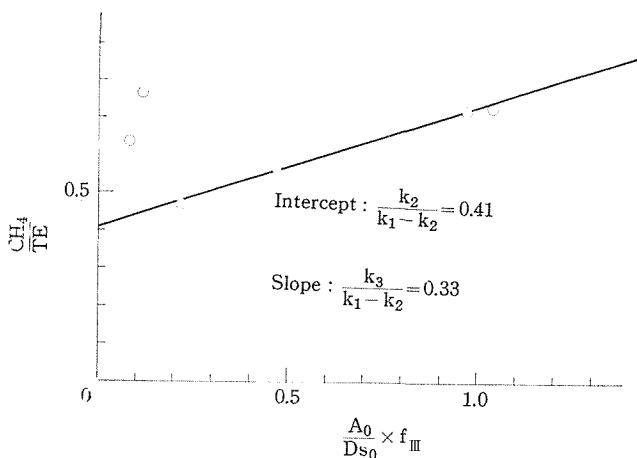Masakazu SUAMA and Yoshimasa TAKEZAKI

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:

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

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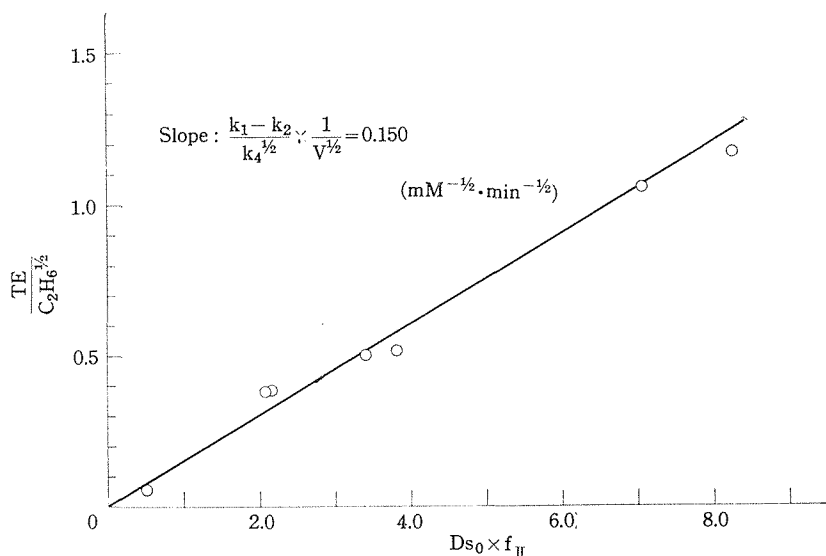

Fig. 7. Linear relationship derived from eq. 10.

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).

Here, when the absolute value of k_4 is taken as 2×10^{13} cm^3. mole^{-1}. sec^{-1}. (1.2×10^9 l. mM^{-1} min.$^{-1}$) from the published papers[10], the relative ratio k_1/k_4 becomes 3×10^{-6} at 100°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°C have been estimated:

$$\frac{k_1}{k_4} = \frac{k(\text{S–S scission by CH}_3)}{k(\text{recombination of CH}_3)} \simeq 3 \times 10^{-6},$$

$$\frac{k_2}{k_3} = \frac{k(\text{H–abstraction from disulfide})}{k(\text{H–abstraction from azomethane})} \simeq 1,$$

$$\frac{k_1}{k_2} = \frac{k(\text{S–S scission by CH}_3)}{k(\text{H–abstraction by CH}_3 \text{ from disulfide})} \simeq 3.4.$$

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°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) CH$_3$SH; L. Vanino "Präparative Chemie" p. 88, Ferdinand Enke, Stuttgart (1937).

(8) CH$_3$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).