Polymerization of Acetylene Photo-Induced by Dimethyl Disulfide

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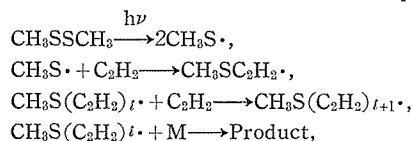
Dimethyl disulfide vapor was photolyzed in the presence of acetylene by 2537 Å light at 40°. Induced polymerization of acetylene of short chain was observed, which was inhibited by small amount of NO.

The pressure change can be expressed by

$$-d\Delta p/dt = I_{abs}(0.0094(C_2H_2) + 4.23) \quad \text{(in mm, min)}.$$

Combining this with the results of product analyses, the following reaction mechanism has been proposed to account for the observation quantitatively:

$$CH_3SSCH_3 \xrightarrow{h\nu} 2CH_3S\cdot,$$
$$CH_3S\cdot + C_2H_2 \longrightarrow CH_3SC_2H_2\cdot,$$
$$CH_3S(C_2H_2)_i\cdot + C_2H_2 \longrightarrow CH_3S(C_2H_2)_{i+1}\cdot,$$
$$CH_3S(C_2H_2)_i\cdot + M \longrightarrow Product,$$

where M is the fine droplets of liquid products suspending in the whole reactor space. The mean kinetic chain length was about 2 under the conditions experimented and the activation energy of the propagation step has been calculated to be 3.2 kcal/mole.

INTRODUCTION

In the previous preliminary paper[1] on the gas phase photolysis of dimethyl disulfide, one of the authors (Y. T.) found that in the presence of acetylene a slight pressure decrease took place (quantum yield was about 5, varying with the condition) and this decrease was reduced remarkably by the addition of NO, and suggested that the reaction was a short chain polymerization of acetylene initiated by the CH_3S radicals produced. In this paper we deal with this reaction in detail; no report on this problem seems to have appeared hitherto except one of Sauer[7].

EXPERIMENTAL

Dimethyl disulfide was prepared as before[1]; $n_D^{20} = 1.5262$ (1.5260^{3}), $d_4^{15} = 1.067$ ($d_4^{18} = 1.046^{4}$), b. p. 42°C at 60mm, g. l. chromatography showed no impurity and no absorption was found in I. R. spectrum other than those specified for CH_3SSCH_3 (1431, 1416, 1304, 955cm^{-1} [5]) and C–H stretchings near 3000cm^{-1}).

Acetylene was produced from carbide and washed in series by NaOH 20% solution, Fe$(NO_3)_3$ + CuSO$_4$ + Hg$(NO_3)_2$ + KCl solution, HgCl$_2$–HCl aq., and NaOH 20% solution and then deoxygenated in a reservoir by alkaline-pyrogallol solution, and dried with silica-gel before each run. By g. s. c. the purity was found to be 98%, the rest being N$_2$ used for purge.

NO was prepared as usual[6] in the atmosphere of N$_2$, passed through H$_2$SO$_4$ and

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KOH solutions and $CaCl_2$ and condensed in a dry-ice trap, then only NO was evaporated and stored; purity was 93% (N_2 7% by g.s.c.).

For the pressure change measurement, 15W hot cathode low pressure mercury lamp operated by 240±5 mA. d.c. at 50°C was used as a light source together with a water filter. The light intensity was varied by means of 7 irises of different hole size. Details of optical system were the same as described before[2].

The reactor was a glass cylinder of 32mmφ×52.5mm (42.3cc) with a quartz window at one side, which was mounted in an electric furnace kept within ±0.01° during the run, and connected through a capillary opening with the evacuation, manometers and reactant reservoir system. Pressure changes were measured by null method as described before[1], that is, the combination of dibutyl phthalate U tube—lamp and photocell—amplifier—zero meter and a plunger of pressure balancing box—variation of the resistance of an arm of a Wheatston's bridge associated with the screw of the plunger—recorder. The overall accuracy of this instrument was 0.001mm Hg/min. Velocity of pressure change was estimated from the difference of the inclination of the points on the chart in between 2 minutes for each dark and lighted period.

For the product analysis, a large glass cylindrical reactor (90mmφ×520mm), was constructed in which the above-mentioned lamp (24.6mmφ×415mm) was enclosed coaxially (net volume 2477cc). After the run gaseous products were withdrawn by a Töpler pump and the liquid products remaining in the vessel were washed with ether or CS_2. Analyses were made mainly by gas chromatography, e.g.,

Gaseous hydrocarbons   g.s.c. No. 1. active carbon 1 m, 100°C, H_2.

CH_3SH and light S compds.   g.l.c. No. 2. dioctyl phthalate 1 m, 56°C, H_2.

CH_3SSCH_3 and liquid S compds.   g.l.c. No. 3. dioctyl phthalate 1 m, 155°C, H_2.

With some samples I.R. (Perkins Elmer-121) and U.V. (Shimadzu QB-50) spectra were taken and micro-elemental analyses were carried out (Analytical Center in Dept. of Pharmaceutics).

RESULTS

The absorption coefficient (natural log., 1/cm mol) of disulfide vapor is reproduced in Fig. 1, each k being the average of observations for 3.0, 4.85 and 7.3mm
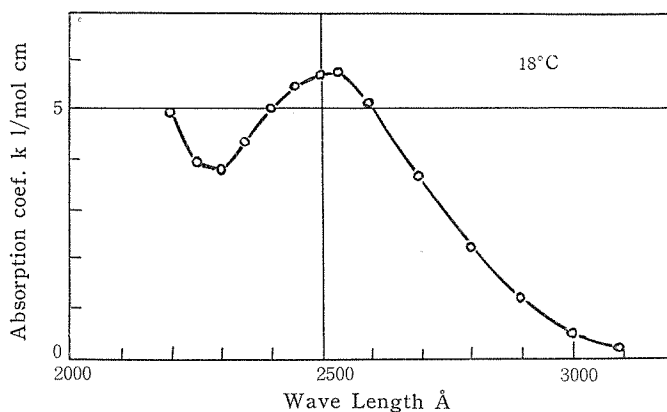

Fig. 1. Absorption coefficient of dimethyl disulfide vapor.

at 18°C in the optical path of 50.0mm. Since only the light of 2537Å is effective in this experiment[3], we use $k_{2537}=5.78\times10^2$ for the calculation of quantum yield in which the I_{abs} is corrected for the reflections of windows by the equations

$$I_{abs}=I_0(1.08x-0.08x^2),$$
$$x=1-exp(-kcd),$$

    c concentration, d optical path length.

The incident light intensities (2537 Å) measured by uranyl oxalate and phototube method were as follows:

Iris No.	1	2	3	4	5	6	7
Hole diameter (mm)	3.67	3.19	2.89	2.44	2.10	1.50	1.03
Area ratio	1	0.755	0.623	0.443	0.329	0.168	0.079
$I_0\times10^8$ Einst/min	3.83	3.02	2.53	1·83	1.38	0.77	0.35
I_0 ratio	1	0.790	0.662	0.481	0.361	0.201	0.091

In order to find out the effect of I_{abs} on the rate, pressure change was observed changing the pressure of dimethyl disulfide, (DMS), under one fixed condition, that is, 38°C, Iris No. 1, C_2H_2 pressure 100 ± 2mm. The rate increased as (DMS) was raised, but as shown in Fig. 2, quantum yield $\Phi_p\equiv-d\mathit{\Delta}p/dt/I_{abs}$ (in pressure) seems
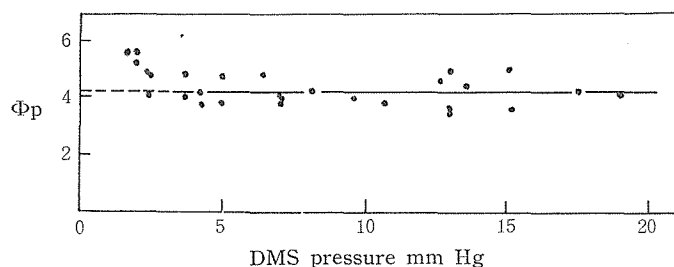

Fig. 2. Effect of DMS pressure on quantum yield of pressure.

to remain constatn between 3—19mm of DMS, the extent of absorption being 39.5 —95% in this reactor. The scatter of points is rather large and the homogeneity of reaction along the light path cannot be assured because of high absorption, but the relation never assumes any other form, e. g., $d\mathit{\Delta}p/dt\propto I^n_{abs}$, $n=1/2$, $3/2$, etc.

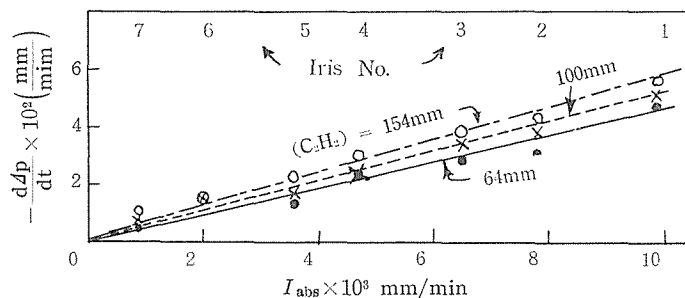The effect of incident light intensity can be seen in Fig. 3, where the intensity

Fig. 3. Effect of light intensity on the rate.

was varied by 7 irises at the fixed amount of DMS, and $(C_2H_2) = 64$, 100, and 154mm.

Within the experimental errors, which are rather large as is seen in Fig. 2, the linear relationship holds.

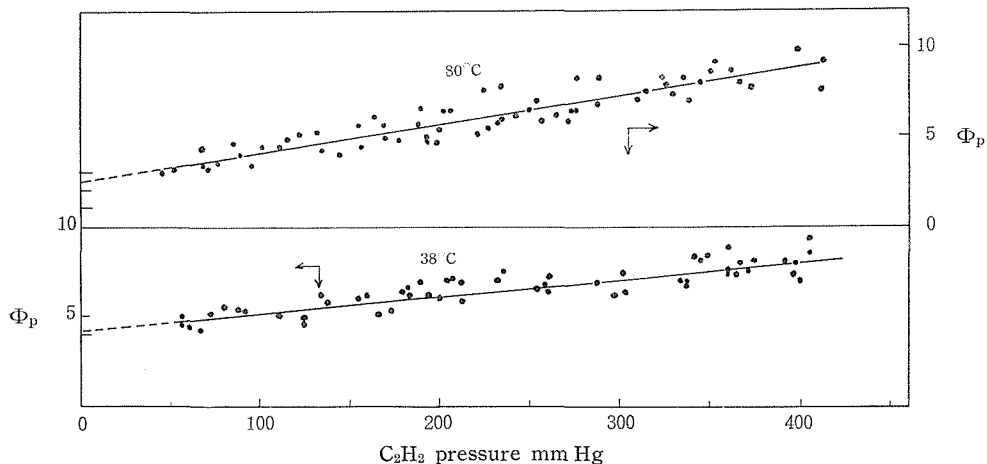The effect of acetylene pressure is shown in Fig. 4 in which the condition is:

Fig. 4. Effect of acetylene pressure on quantum yield of pressure.

$(DMS) = 3.6mm$, Iris No. 1, $38°$ and $80°$, and $(C_2H_2) = 5 - 400mm$. By means of the least squares we get the most probable relations,

$$\left. \begin{array}{l} \Phi_p = 0.0094(C_2H_2) + 4.23 \text{ at } 38° \\ \quad = 0.016 \ (C_2H_2) + 2.52 \text{ at } 80° \quad (C_2H_2) \text{ is expressed in mm.} \end{array} \right\} \text{ (I)}.$$

At one same condition, i.e., $38°$, $(DMS) = 3.6mm$, and $(C_2H_2) = 100mm$, Φ_p is 4.2, 5.2 and 5.2, respectively from Figs. 2 and 3 and (I).

Thus the rate of pressure drop is proportional to the rate of light absorption, linear to acetylene pressure, and independent of DMS pressure except for light absorption.

Inhibition by NO addition is given in Fig. 5; the condition is: (DMS) 10.7mm, (C_2H_2) 152mm, Iris No. 1, $38°C$ and (NO) $0.1 - 3mm$.
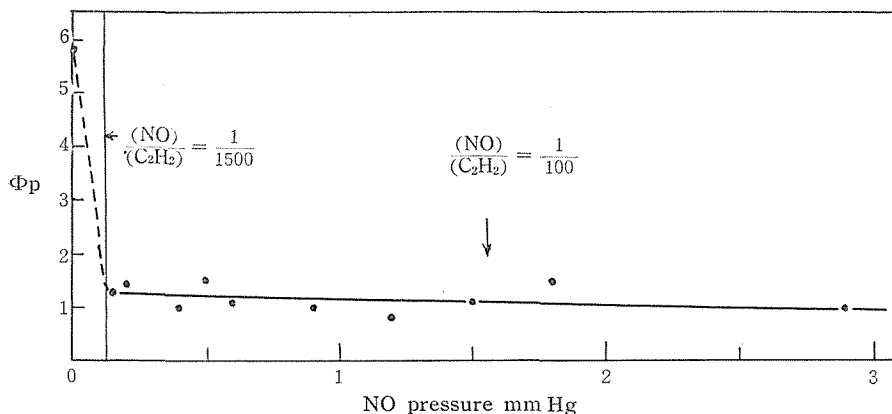

Fig. 5. Effect of NO addition.

Trace of NO (amounts to 1/1500 of acetylene) is sufficient to reduce the rate down to $\Phi_p = 1$ which may be explicable if we assume that $CH_3S + NO \rightarrow CH_3SNO$ is exclusively fast and CH_3SNO is volatile under the experimental condition. When the irradiation was continued further in the presence of NO the time (t') could be observed when the $d\Delta p/dt$ attained the rate of no NO addition; some examples are given below, but these figures are by no means exact and no quantitative measurement was made:

(NO) mm	0.019	0.045	0.120
t′ min	8	16	>25.

In order to test the possibility that the diffusion to the wall would contribute the rate, N_2 was added to the reaction mixture up to 450mm, but no trend could be observed.

In the large reactor we observed a remarkable mist formation soon after the commencement of irradiation, which at first started in the space around the lamp, convecting slowly, then spreaded in the whole volume of the reactor during the irradiation.

The particle of the mist was quite fine at first but gradually grew; in 1 hr after the run the mist sticked entirely on the wall or sedimented to the bottom. The amount of liquid was about one drop. In the reactor for pressure measurement in which the light intensity was much lower than the above, no mist was observed but a faint scattering of light (Tyndall phenomenon) was recognized.

The analyses of products which were withdrawn from the large reactor (DMS 1.3−12.6mm, C_2H_2 113−346mm, exposure 15−30 min, total photon emitted from the entire surface of the lamp 1.74×10^{-4} Einst/min) were as follows:

CH_4 $\Phi = 0.053$ and 0.076; C_2H_6, C_2H_4, C_3H_8 or C_3H_6 is absent by g.s.c.; CH_3SH and H_2S absent, and two unknown peaks were observed after the appearance of CH_3SH in g.l.c. No. 2, each amount being estimated roughly as twice that of CH_4 merely by comparing peak areas.

In the liquid product, after evaporation of the solvent ether or CS_2 used to collect the sample, presence of $CH_3SCH = CHSCH_3$ (identified by authentic sample synthesized by us) was found together with DMS and two unknown substances by g.l.c. No. 3.
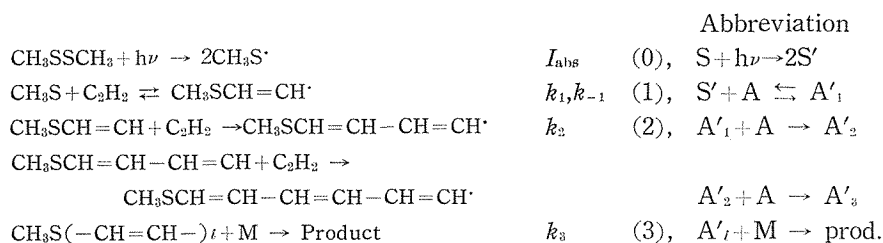
U.V. spectrum of the liquid (mixture of products and some DMS) showed the absorption near 2360 Å after corrected for the absorption of DMS, this might be due to the presence of conjugated double bonds; the mean composition corresponded to $C_{4.2}H_{7.7}S_2$ by elementary analysis but when the light intensity was rebuced by lowering d.c. current and covering the lamp with metal net, the C/S and H/S values were raised, $viz.$, $C_{5.2}H_{8.5}S_2$.

I.R. absorption coincided with those of DMS and $CH_3SCH = CHSCH_3$, but some other unidentified weak absorptions were found.

Summing up these observations it would be concluded that no gaseous product is present except only minute amount of CH_4, and the products are all liquid in which some DMS is dissolved and the mean formula is about $C_4H_8S_2$, so the mixture is supposed to be composed of some rather highly unsaturated sulfur containing compounds, one of which is $CH_3SCH = CHSCH_3$.

DISCUSSION

In order to account for the observed facts we propose the following scheme:

			Abbreviation
$CH_3SSCH_3 + h\nu \rightarrow 2CH_3S\cdot$	I_{abs}	(0),	$S + h\nu \rightarrow 2S'$
$CH_3S + C_2H_2 \rightleftarrows CH_3SCH=CH\cdot$	k_1, k_{-1}	(1),	$S' + A \rightleftarrows A'_1$
$CH_3SCH=CH + C_2H_2 \rightarrow CH_3SCH=CH-CH=CH\cdot$	k_2	(2),	$A'_1 + A \rightarrow A'_2$
$CH_3SCH=CH-CH=CH + C_2H_2 \rightarrow$			
$\quad\quad CH_3SCH=CH-CH=CH-CH=CH\cdot$			$A'_2 + A \rightarrow A'_3$
$CH_3S(-CH=CH-)_l + M \rightarrow$ Product	k_3	(3),	$A'_l + M \rightarrow$ prod.

where M is the droplets of mist in the reactor.

Formation of CH_3S radical on irradiation of DMS would be most probable[1]. Recombination of CH_3S is eliminated because the intervention of this reaction leads to the overall rate equation which is incompatible with the observation.

A number of papers[7] have been presented on the addition of thiyl radicals to olefins and the reversibility of this reaction, particularly as regards the chain transfer in high polymerization. The initiation (1) and chain propagation (2) would not need further comments.

The termination step (3) is assumed in order to explain the observation that the rate of pressure change is proportional to the first power of I_{abs}, linear to acetylene and independent of DMS pressure. The mechanism which leads to this required equation should be of the first order in termination if (1) and (2) is assumed. Bimolecular terminations such as $CH_3S + A'_l \rightarrow$ product and $A'_l + A'_{l \text{ or } j} \rightarrow$ product are necessarily ruled out.

One conceivable unimolecular termination may be wall termination, but the experiment of innert gas addition showed no positive indication, meanwhile we observed a remarkable mist formation during the run, so we assume that growing radicals migrate into the droplet on collision in the whole space of the reactor and then stabilize through, e. g., dimerization, the rate determining step being collision. The constancy of k_3 will be shown later. Since no CH_3SH and C_2H_6 is formed and ΦCH_4 is quite small, we have omitted the H abstraction by $CH_3S\cdot$ and $CH_3SSCH_3 \rightarrow 2CH_3 + S_2$. We assume the rate constant of each addition step is independent of the size of growing chain radicals.

Now applying steady state method, we have

$$(S') = 2I_{abs}[1 + k_{-1}/(k_2(A) + k_3)],$$

$$(A'_l) = 2I_{abs}[k_2(A)^{l-1}/(k_2(A) + k_3)^l],$$

$$\left(\sum_1^\infty A'_l\right) = 2I_{abs}/k_3,$$

and, since the product in the droplet does not contribute to the gas pressure,

$$\frac{-d\Delta p}{dt} = \frac{-d(S)}{dt} + k_1(S')(A) + k_2\left(\sum_1^\infty A'_l\right)(A)$$

$$= I_{abs}\{(3 + 2k_{-1}/(k_2(A) + k_3) + 2k_2(A)/k_3\}$$

$$\text{(II)}$$

This equation agrees well with the observed relation (I) ; according to this me-chanism $2k_{-1}/(k_2(A)+k_3)$ should be $4.2-3=1.2$ at $38°$, but at $80°$ k_{-1} becomes negative; considering the somewhat larger error in the measurements and the observed dissolution of DMS vapor into the droplet, the values of this ratio is not so reliable.

The mean chain length, ν, is then given by

$$\nu = \frac{-d(A)/dt}{2I_{abs}} = 1 + k_2(A)/k_3,$$

and from the relation (I) at $38°$ we get $\nu=1+0.0047(A)$, for example $\nu=1.5$ and 2, for $(A)=100$mm and 200mm, respectively.

From the slopes of the relation (I), the difference of activation heat of (2) and (3) is obtained, $viz.$, $E_2-E_3=2.7$kcal/mol. Since E_3, which corresponds to the apparent tempreature coefficient of collision to the droplets, is about 0,5 kcal at these tempe-ratures, we have $E_2=3.2$kcal/mol as the activation heat of propagation.

Now, the constancy of k_3 has to be proven; since the rate of collision should be dependent of the surface area of droplets which would increase during the irradi-ation by the accumulation of products, we have to show that the change of k_3 with time can be neglected at least in the period of the pressure measurement.

The calculation is performed under the following condition: DMS 3.6mm, reactor volume 44.1cc, $38°$, C_2H_2 200mm, $I_{abs}=3.83\times10^{-8}\times0.445$ Einst/min $=8.8\times10^{10}$ photon /seccc.

We assume that M spherical particles of the mist are present in one cc at the begining of the pressure change measurement (t_1 from the commencement of irradi-ation, actually kept constant at 10 sec) and that this number does not change during the observation.

The size of particles is reprsented by d, S and V, respectively for diameter, surface area and volume with suffix 1 for those at t_1, and suffix 2 for those at the end of measurement, t_2, t_2-t_1 being usually 120 sec.

Number of added product molecules to a growing particle is denoted by m for each particle and the mean size of the product is estimated to be $CH_3S(CH=CH)_4$ SCH_3, M. Wt. $=198$ ($\nu=2$ and product is assumed to be the dimer of A'_2), and specific gravity is taken as unity by analogy to $CH_3SCH=CHSCH_3$ and $CH_3SC_4H_8SCH_3$ (synthesized in this laboratory).

The volume and the surface area of one particle at the time when m product molecules has accumlated are

$$V=V_1+mw/\rho \quad \text{and} \quad S=\pi[6(V_1+mw/\rho)/\pi]^{2/3},$$

where w is the mass of one molecule, $i.\ e.$, 198/Avogadro number, and ρ is the specific gravity ($=1$).

The number of radicals which hit the surface of droplets in unit volume and time, Z, which is equivalent to the rate of radical disappearance, is expressed by

$$Z=-dN/dt=MSN(kT/2\pi m_r)^{1/2}=k_3N,$$

where N is the number of radicals in unit volume, k Boltzmann constant and m_r the mass of one radical ($=99$/Avogad. no.), and the efficiency of condensation is assumed to be unity, this assumption is the most unfavorable for the constancy of k_3. The ratio of k_3 at t_1 and t_2 is given by

$$k_{3t2}/k_{3t1} = S_2/S_1 = (V_2/V_1)^{2/3} = (1+mw/\rho V_1)^{2/3}.$$

On the other hand the rate of growth of the particle is represented by

$$\frac{dm}{dt} = -\frac{dN}{dt} \cdot \frac{1}{2M} = \frac{MSN(kT/2\pi m_r)^{1/2}}{2M}$$

$$= \frac{\pi^{1/3} 6^{2/3}(V_1+mw/\rho)^{2/3}N(kT/2\pi m_r)^{1/2}}{2}.$$

Integration between t_1 and t_2 leads to

$$\alpha(t_2-t_1) = \frac{3\rho}{W}\left\{(V_1+mw/\rho)^{1/3} - V_1^{1/3}\right\} = \frac{3\rho V_1^{1/3}}{W}\left\{(1+mw/\rho V_1)^{1/3}-1\right\},$$

where $\alpha = \pi^{1/3} 6^{2/3} N(kT/2\pi m_r)^{1/2}/2$

Hence,

$$\frac{k_{3t2}}{k_{3t1}} = \left\{\frac{\alpha(t_2-t_1)w}{3V_1^{1/3}\rho}+1\right\}^2$$

and if k_3 does not vary appreciably as expected,

$$k_{3t2}/k_{3t1} \fallingdotseq 1 + 2\alpha w(t_2-t_1)/3\rho V_1.$$

In order to calculate this we have to know the order of magnitude of N ; this can be given from

$$N = \sum(A'_i) = 2I_{abs}/k_3 = 2\times 3.9\times 10^{12}/k_3 \quad (molec.\ cc^{-1})$$

and to find the approximate magnitude of k_3 we refer to (I) and (II), and get

$$2k_2/k_3 = 0.0094 \quad (mm^{-1}) = 3.02\times 10^{-19} \quad (cc.\ molec.^{-1})$$

and estimate the value of k_2 by assuming the pre-exponential factor to be analogous to that of $CH_3+C_2H_4$[8], *i. e.*,

$$k_2 = 10^{11}e^{-3200/RT}(cc\ mol^{-1}\ sec^{-1})$$

$$= 9.56\times 10^{-16} \quad (cc\ molec^{-1}\ sec^{-1}).$$

Hence,

$$k_3 \fallingdotseq 6.3\times 10^3 \quad (sec^{-1})$$

and accordingly

$$N \fallingdotseq 1.2\times 10^9 \quad (cc^{-1}).$$

Introduction of numerical values given heretofore yields

$$k_{3t2}/k_3t_1 = 1+5.0\times 10^{-7}/V_1^{1/3}$$

and the condition that k_{3t2} remains constant within 5% of k_{3t1} is $V^{1/3}_1 > 10^{-5}$ and accordingly $d_1 > 124\mu\mu$, and $d_1 > 626\mu\mu$ for 1% error.

Since we could recognize faint Tyndall phenomenon the particle size would be of the order of $d=100\mu\mu$, so the constancy of k_3 may be expected to be plausible.

Finally the apparent discrepancy between the calculated mean product composition $CH_3S(CH=CH)_4SCH_3$ from $\nu=2$ and the observed elemental analysis $C_{4\sim5} H_{8\sim9} S_2$ may be caused partly by the dissolved DMS in the product as found by g. l. c. and partly by the difference in the conditions between the pressure measurement run and analysis run, in the latter case the incident density of light is about 100-fold

large. One reason for this is that a trend was seen to increase C/S and H/S of products in the run where the intensity of light was reduced (cf. previous section). As the equation for ν involves no term of light intensity, other different steps not included here, e. g., $CH_3S + A'_i \rightarrow CH_3SA'_i$ (in the droplet), might contribute under high concentration of CH_3S.

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