PHOTOLYSIS OF DIMETHYL ETHER BY 184.9 nm RADIATION

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Summary

The photolysis of dimethyl ether (DME) by 184.9 nm radiation at room temperature was studied. The products CH_4, C_2H_6, CH_3OH, $CH_3OC_2H_5$, $CH_3OCH_2OCH_3$, $(CH_3OCH_2)_2$ and $CH_3O_2CH_3$ were identified and their quantum yields were determined as a function of the DME pressure in the range 5.3 - 46.6 Torr. The results of a scavenging experiment with NO and photolysis of the mixture of DME and DME-d_6 led to the conclusion that the photolysis proceeds dominantly through a radical process of CH_3—OCH_3 fission. The quantum yield $\phi(CH_3)$ of the primary process was estimated to be nearly unity from the calculation of the final product yields.

1. Introduction

The photochemistry of alkyl ethers in the vacuum UV region has been reported by several workers. Harrison and Lake [1] reported a study of the photolysis of various alcohols, ethers and ketones by radiation below 192 nm from a hydrogen discharge lamp. In the photolysis of methanol and dimethyl ether (DME) they found that a large amount of formaldehyde was formed by IR absorption. To explain the formation of formaldehyde, Calvert and Pitts [2] proposed the following two processes:

$$CH_3OCH_3 + h\nu \longrightarrow CH_3O \text{ (or } HCHO + H) + CH_3$$
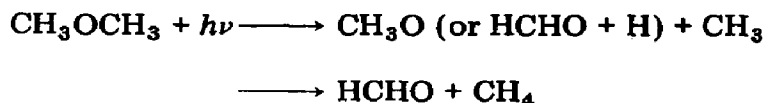
$$\longrightarrow HCHO + CH_4$$

Meagher and Timmons [3] studied the photolysis of DME by 147.0 nm radiation. They found hydrogen, HCHO, CH_4 and C_2H_6 as the main products, but no formation of methanol was observed. In view of this result they concluded that the fission of the C—O bond of DME does not take place with 147.0 nm radiation. Considering the pressure dependence of the quantum yields of the products, they assumed that two competing primary processes were involved: one is a rapidly dissociating process and the other is a slower

process. Mercury-photosensitized decomposition of DME has been studied in detail by several workers [4 - 6], and it has been established that hydrogen abstraction by excited mercury atoms is the dominant primary process.

The photolysis of higher alkyl ethers in the liquid phase by 184.9 nm radiation has been studied extensively and reviewed by von Sonntag et al. [7 - 9]. They confirmed that the major primary process in the photolysis of diethyl ether and t-butyl methyl ether is C—O bond fission.

In the present study we investigated the photolysis of DME by 184.9 nm radiation. The first absorption band below 200 nm is assigned to the $n-\sigma^*$ transition for DME and other alkyl ethers [10], and we may expect the photochemical behavior at 184.9 nm to be different from that at 147.0 nm. Actually we confirmed that the primary process of DME with 184.9 nm radiation is mainly C—O bond fission in contrast to the C—H bond fission obtained with 147.0 nm radiation. The quantum yield of C—O bond fission is nearly unity, which indicates that this reaction is a good source of methoxy radicals. As well as the primary photochemical process of DME, we investigated several secondary reactions which involved CH_3, CH_3O and CH_3OCH_2 radicals.

2. Experimental

2.1. Apparatus

The vacuum line and the gas-handling system were conventional but precautions were taken to keep the system mercury free. The quartz reaction cell was a cylinder of diameter 5 cm and length 5 cm with volume about 113 ml. A low pressure mercury lamp of the swirl type was used for the 184.9 nm radiation. The external temperature of the electrode was kept constant at 40 °C by circulating water. The total input of photons was determined by N_2O actinometry [11] to be 7.2×10^{14} photon s^{-1} for one lamp and 1.4×10^{15} for another lamp used in some experiments. Nitrogen flowed between the reaction cell and the lamp to prevent the absorption of the 184.9 nm light by oxygen and no filter was used. The pressure of DME in the reaction cell was determined by a Pyrex Bourdon gauge calibrated by a mercury manometer.

2.2. Materials

The DME was obtained from the Matheson Co. and was purified by trap-to-trap distillation. For the analysis of dimethyl peroxide, DME of higher purity was prepared by gas chromatographic (GC) separation, since the original DME contained some unidentified impurities which gave small GC peaks having retention times comparable with that of dimethyl peroxide. The DME-d_6 was obtained from the Merck Sharp & Dohme Canada Co. Dimethyl peroxide for the standard sample was synthesized from H_2O_2 and $(CH_3)_2SO_4$ [12].

2.3. Procedure

The irradiation time was normally 5000 s and the conversion of DME was kept to less than 2%. All experiments were performed under conditions of complete photon absorption. After irradiation the reaction system was connected to an evacuated GC sampling cell of volume about 10 ml, and part of the reaction mixture was sampled by free expansion to the cell. The amounts of CH_4, C_2H_6, CH_3OH and $CH_3O_2CH_3$ present were determined by GC using this sampling procedure. The relative retention times of these compounds normalized to DME with a 3 m Porapak-Q column at 65 °C with a helium carrier were as follows: CH_4, 0.56; C_2H_6, 0.15; CH_3OH, 2.03; $CH_3O_2CH_3$, 3.19. The rest of the reaction mixture was transferred to another evacuated GC sampling cell at liquid-nitrogen temperature and subjected to GC analysis, the column temperature being raised to 140 °C. $CH_3OC_2H_5$ (ethyl methyl ether), $CH_3OCH_2OCH_3$ (dimethoxymethane) and $(CH_3OCH_2)_2$ (dimethoxyethane) were identified by comparing the retention times of these compounds with those of standard samples (the relative retention times normalized to DME: $CH_3OC_2H_5$, 2.40; $CH_3OCH_2OCH_3$, 5.20; $(CH_3OCH_2)_2$, 20.0) and by mass spectrometric (MS) analysis of separated fractions at low electron impact energy. The determination of the amounts of products is mainly made by flame ionization detection (FID) on the basis of the sensitivity calculated from the reported effective carbon number. Since the effective carbon number for dimethyl peroxide is not known, we determined its sensitivity for thermal conductivity detection (TCD) using the formula for sensitivity given by Messner et al. [13], and the sensitivity of FID for dimethyl peroxide was determined from the ratio of peak area for TCD to that for FID in the successive passage through TCD and FID. (The amount of dimethyl peroxide in the reaction mixture was so small that it could be determined only by FID.)

3. Results and discussion

3.1. Quantum yields of products

Irradiation of DME with 184.9 nm light at room temperature produced CH_4, C_2H_6, CH_3OH, $CH_3OCH_2CH_3$, $CH_3OCH_2OCH_2OCH_3$, $CH_3O_2CH_3$ and $(CH_3OCH_2)_2$. The amounts of these products were proportional to the irradiation time. A small amount of hydrogen was also detected, but it was concluded that it was formed by the secondary photolysis of accumulated primary products (probably formaldehyde) as its rate of production increased rapidly with irradiation time. The quantum yields of the products at various DME pressures are given in Table 1. Above 10 Torr the quantum yields are almost independent of DME pressure, while below 10 Torr some increase of $\phi(CH_4)$ and $\phi(C_2H_6)$ and decrease of $\phi(CH_3OC_2H_5)$ were observed. The behavior of $\phi(CH_4)$ at lower pressure will be discussed in Section 3.5. In addition to the products listed earlier, HCHO was also a product and we tried to determine its amount by the chromotropic acid method. Unfortunately, the

TABLE 1

Quantum yields of products

Pressure of DME (Torr)	$\phi(CH_4)$	$\phi(C_2H_6)$	$\phi(CH_3OH)$	$\phi(CH_3OC_2H_5)$	$\phi(CH_3OCH_2OCH_3)$	$\phi((CH_3OCH_2)_2)$	$\phi(CH_3O_2CH_3)$
5.3	0.11	0.36	0.41	0.23	0.10	0.013	–
8.3	–a	–	–	–	–	–	0.0073
10.2	–	–	0.46	0.31	0.11	0.025	–
15.1	0.069	0.30	0.42	0.33	0.079	0.020	–
16.5	–	–	–	–	–	–	0.0075
25.2	0.051	0.35	0.57	0.32	0.068	0.036	–
26.3	–	–	–	–	–	–	0.0065
29.1	0.050	0.33	0.61	0.36	0.058	0.046	–
39.2	0.051	0.34	0.54	0.33	0.046	0.043	–
46.6	0.035	0.34	0.54	0.33	0.048	0.051	–

a Not determined.

solution treated with chromotropic acid was brown, and the reliable determin-
ation of the amount of HCHO was unsuccessful. The brown color of the
solution may be due to the oxidation of chromotropic acid by the presence
of dimethyl peroxide in the mixture of products.

3.2. Effect of NO addition

The formation of CH_4, C_2H_6 and $CH_3OC_2H_5$ was completely suppressed
by the addition of 1 Torr NO in 10 Torr DME which indicates that CH_3
radicals were scavenged by NO while the yield of methanol was not affected
by the addition of NO up to 2.5 Torr. The molecular formation of CH_3OH
may be one possible explanation, but it is unlikely that all the methanol is
formed through molecular processes. The following disproportionation
reactions catalyzed by NO which were suggested by Knight and Gunning
[14] may be a more probable process of formation of CH_3OH:

$$CH_3O + NO \longrightarrow CH_3ONO$$

$$CH_3ONO + CH_3O \longrightarrow CH_3OH + HCHO + NO$$
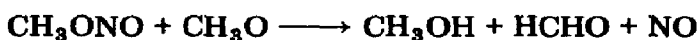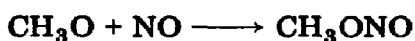
3.3. Photolysis of a mixture of DME and DME-d_6

In order to clarify whether or not the molecular mechanism is involved
as a primary process, a crossover experiment was carried out with a mixture
of DME and DME-d_6 using 184.9 nm irradiation and the determination of
the isotope distribution of d-substituted ethyl methyl ether and methanol as
products was attempted. To determine the relative abundance of d-substituted
products, the fractions of ethyl methyl ether and methanol were isolated by
GC and subjected to MS analysis. The results for ethyl methyl ether are
shown in Table 2. The electron accelerating voltage of the MS was reduced
to as low a value as possible to suppress the superposition of a fragment ion
peak formed from a parent ion of higher molecular weight on a parent ion
peak of lower molecular weight. The values of the electron accelerating volt-

TABLE 2

Isotope distribution (%) of methyl ethyl ether

Pressure of DME[a]		Electron energy[b] (eV)	m/e								
P_{h-6} (Torr)	P_{d-6} (Torr)		60	61	62	63	64	65	66	67	68
12	22	12	20	4	18	29	4	4	2	4	14
14	20	7	27	2	11	33	2	9	0	0	15
13	20	5	30	2	8	36	2	9	0	0	13

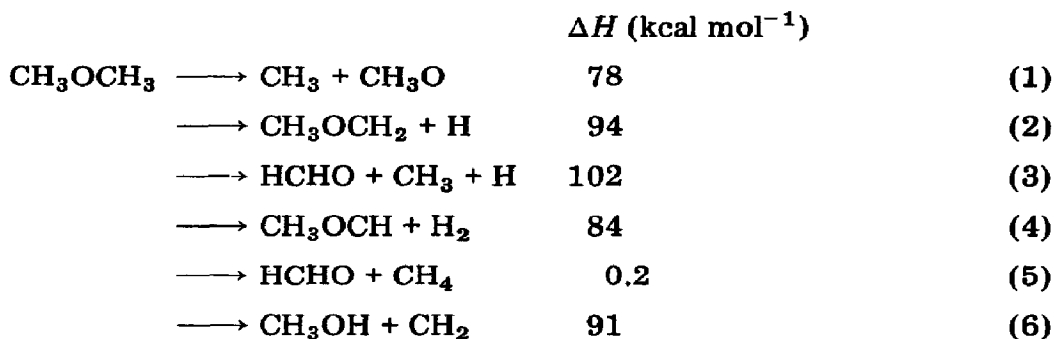[a]Pressure of DME isotope mixture in the photolysis.
[b]Electron accelerating voltage obtained as a nominal reading on a voltmeter on the mass
spectrometer.

age shown are a nominal reading on a voltmeter on the MS without calibration, and the actual electron energy is probably higher by 1 or 2 eV. If we assume that ethyl methyl ether is formed exclusively through the recombination of the methyl radical with the methoxymethyl radical, the products expected in the isotope crossover experiment are $CH_3OC_2H_5$ (m/e = 60 for the parent ion), $CH_3OCH_2CD_3$ (m/e = 63), $CD_3OCD_2CH_3$ (m/e = 65) and $CD_3OCD_2CD_3$ (m/e = 68). The results of the MS analysis clearly show the dominant presence of these four products, which supports the assumed radical recombination process. The lower abundance of m/e = 65 and m/e = 68 peaks compared with m/e = 63 and m/e = 60 peaks may be due to the isotope effect in the abstraction process of DME which gives the CH_3OCH_2 radical. The relatively large abundance of the m/e = 62 peak which persists even at a (nominal) electron accelerating voltage of 5 eV is disturbing. It is probable that the fragment ion $CH_3OCHCD_3^+$ makes some contribution to this abundance, but it should be noted that the m/e = 66 peak ($CD_3OCDCD_3^+$) disappears completely at an electron energy of 7 eV. This result suggests the possible presence of $CH_3OCD_2CH_3$ or $CH_3OCH_2CD_2H$ which are supposed to be formed through the insertion of CD_2 into DME-h_6, although the formation of their counterparts $CD_3OCH_2CD_3$ or $CD_3OCD_2CH_2D$ was not observed.

We would also expect to be able to decide from the isotope distribution in the mass spectogram of methanol whether or not molecular formation of methanol ($CH_3OCH_3 \longrightarrow CH_3OH + CH_2$) could take place. Unfortunately, CH_3OD and CD_3OD exchange their D atom(s) quite easily with H atoms derived from the glass walls of either the vacuum line of the reaction system or the sample-introducing system of the MS, and the peak at m/e = 36 corresponding to CD_3OD was not observed. This exchange reaction was also confirmed in the photolysis of pure CD_3OCD_3, where the formation of pure CD_3OD was expected but the peak at m/e = 36 was also not observed.

3.4. Reaction mechanism

The elementary reactions of the primary processes considered are as follows:

$$\Delta H \text{ (kcal mol}^{-1})$$

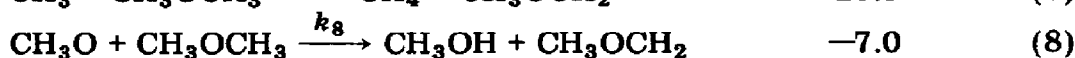|		
$CH_3OCH_3 \longrightarrow CH_3 + CH_3O$	78	(1)
$\longrightarrow CH_3OCH_2 + H$	94	(2)
$\longrightarrow HCHO + CH_3 + H$	102	(3)
$\longrightarrow CH_3OCH + H_2$	84	(4)
$\longrightarrow HCHO + CH_4$	0.2	(5)
$\longrightarrow CH_3OH + CH_2$	91	(6)

The most probable primary process is obviously reaction (1). Since the formation of hydrogen is negligible, reactions (2), (3) and (4) which yield

atomic or molecular hydrogen are unlikely. Molecular formation of CH_4 (reaction (5)) is also less likely considering that the formation of CH_4 is completely suppressed by the addition of NO. On the basis of the present experimental results (NO addition experiment and isotope crossover experiment) molecular formation of methanol and CH_2 (reaction (6)) cannot be entirely excluded, but it is quite certain that most of the primary process proceeds through the C—O bond fission process.
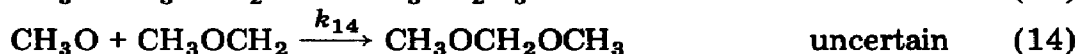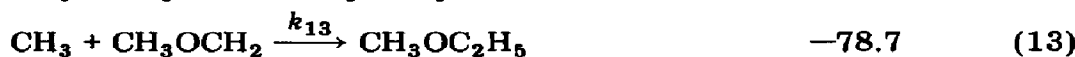
As secondary processes we considered the following four groups of reactions:

$\Delta H(\text{kcal mol}^{-1})$

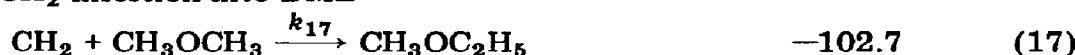(a) H abstraction from DME by CH_3 or CH_3O

$$CH_3 + CH_3OCH_3 \xrightarrow{k_7} CH_4 + CH_3OCH_2 \qquad -10.9 \qquad (7)$$

$$CH_3O + CH_3OCH_3 \xrightarrow{k_8} CH_3OH + CH_3OCH_2 \qquad -7.0 \qquad (8)$$

(b) radical–radical recombinations

$$2CH_3 \xrightarrow[(M)]{k_9} C_2H_6 \qquad -84.2 \qquad (9)$$

$$2CH_3O \xrightarrow{k_{10}} CH_3O_2CH_3 \qquad -34.0 \qquad (10)$$

$$2CH_3OCH_2 \xrightarrow{k_{11}} (CH_3OCH_2)_2 \qquad -71.4 \qquad (11)$$

$$CH_3 + CH_3O \xrightarrow{k_{12}} CH_3OCH_3 \qquad -78.0 \qquad (12)$$

$$CH_3 + CH_3OCH_2 \xrightarrow{k_{13}} CH_3OC_2H_5 \qquad -78.7 \qquad (13)$$

$$CH_3O + CH_3OCH_2 \xrightarrow{k_{14}} CH_3OCH_2OCH_3 \qquad \text{uncertain} \qquad (14)$$

(c) H abstraction from CH_3O by a radical

$$CH_3O + CH_3 \xrightarrow{k_{15}} HCHO + CH_4 \qquad -77.9 \qquad (15)$$

$$CH_3O + CH_3O \xrightarrow{k_{16}} HCHO + CH_3OH \qquad -78.0 \qquad (16)$$

(d) CH_2 insertion into DME

$$CH_2 + CH_3OCH_3 \xrightarrow{k_{17}} CH_3OC_2H_5 \qquad -102.7 \qquad (17)$$

Of our identified products, C_2H_6, $CH_3O_2CH_3$, $CH_3OCH_2OCH_3$ and $(CH_3OCH_2)_2$, are definitely formed through radical–radical recombination processes, but for the formation of $CH_3OC_2H_5$ there is also the possibility of CH_2 insertion into DME (reaction (17)) as described in Section 3.3.

If we assume that C_2H_6, $CH_3O_2CH_3$, $CH_3OC_2H_5$, $CH_3OCH_2OCH_3$ and $(CH_3OCH_2)_2$ are all formed through radical–radical recombination processes, we obtain the following relation:

$$\frac{R(CH_3OC_2H_5)}{R(CH_3OCH_2OCH_3)}\left(\frac{R(CH_3O_2CH_3)}{R(C_2H_6)}\right)^{1/2} = \frac{k_{13}}{k_{14}}\left(\frac{k_{10}}{k_9}\right)^{1/2} \qquad (1)$$

Substituting the experimental values into the left-hand side rates, we find that this ratio is 1.6 at 25.2 Torr, 1.5 at 15.1 Torr and 5.1 at 5.3 Torr. Since all four processes are radical–radical recombination reactions, we can assume that the activation energies of the rate constants are all zero, and the experimental value of nearly unity for the ratio for eqn. (1) is acceptable. The increase of the ratio at lower pressures may be caused by some other process not included in this equation.

3.5. Quantum yield of the primary process

The quantum yield $\phi(CH_3)$ of CH_3 can be calculated by the following relation, neglecting the formation of CH_2 as a primary process:

$$\phi(CH_3) = \phi(CH_4) + 2\phi(C_2H_6) + \phi(CH_3OC_2H_5)$$

We found that $\phi(CH_3)$ is nearly unity, and its variation with DME pressure (Fig. 1) shows no appreciable pressure dependence. In the present reaction system the quantum yield of DME formed by the recombination of CH_3 with CH_3O is assumed to be negligible. However, in spite of this neglect we obtained a quantum yield of nearly unity for CH_3.

It is interesting that a slight increase of $\phi(CH_4)$ is observed at 5.3 Torr of DME, since we would expect $\phi(CH_4)$ to decrease with decreasing pressure of DME if CH_4 is formed exclusively through abstraction from DME by the CH_3 radical. This pressure effect may be due to the enhancement of the dis-proportionation reaction (15)[†] caused by an increase of the stationary concentration of CH_3 and/or CH_3O radicals or an increase of reactivity of either radical, because from the energetic consideration it is expected that a hot radical reaction may be involved under low pressure conditions.
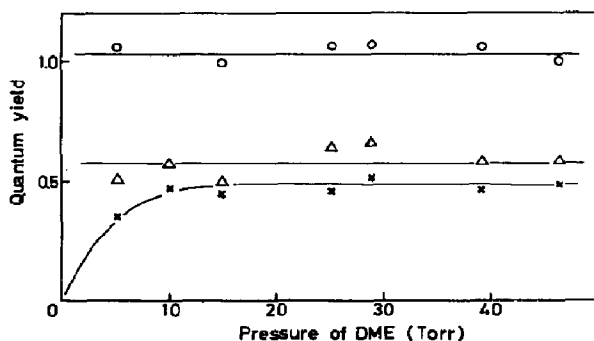

Fig. 1. The variation of $\phi(CH_3)$, $\phi(CH_3O)$ and $\phi(CH_3OCH_2)$ with pressure of DME: $\circ$, $\phi(CH_3)$; $\triangle$, $\phi(CH_3O)$; $\times$, $\phi(CH_3OCH_2)$. $\phi(CH_3O)$ is calculated as a sum of $\phi(CH_3OH)$, $\phi(CH_3OCH_2OCH_3)$ and $2\phi(CH_3O_2CH_3)$, since $\phi(HCHO)$ is not determined. See Section 3.5 of the text.

[†]Thynne and Gray [15] estimated that the ratio of disproportionation ($CH_3 + CH_3O \rightarrow CH_4 + HCHO$) to recombination ($CH_3 + CH_3O \rightarrow DME$) is 1.5 and is independent of reaction temperature in the decomposition of $CH_3O_2CH_3$ in the presence of methyl formate.

Following the same procedure as in the case of CH_3, we can calculate the primary quantum yield of CH_3O if we know the quantum yields of all the final products which contain primary CH_3O or which are derived from the primary CH_3O radical (*e.g.* HCHO). In the present experiment we determined the quantum yields of CH_3OH, $CH_3O_2CH_3$ and $CH_3OCH_2OCH_3$, but not that of HCHO. Assuming that these four species are only products which originate from the primary CH_3O radical, we obtain the following relation:

$$\phi(CH_3O) = \phi(CH_3OH) + 2\phi(CH_3O_2CH_3) + \phi(CH_3OCH_2OCH_3) + \phi(HCHO)$$

$$= \phi(CH_3) \approx 1$$

From the present experimental results we found that the sum of the experimentally determined quantum yields of the three identified products (CH_3OH, $CH_3O_2CH_3$ and $CH_3OCH_2OCH_3$) is 0.58 which shows a defect of 0.42. This defect may correspond to $\phi(HCHO)$, which is not determined in the present experiment.

The quantum yield of CH_3OCH_2 shown in Fig. 1 is not so meaningful since this is the secondary radical formed by the abstraction of DME with CH_3 or CH_3O, but it is included to show that its quantum yield is almost constant with varying DME pressure, decreasing only in the low pressure region.

3.6. The ratio of the rate constants of disproportionation to recombination of the CH_3O radical

Since we have been able to determine the quantum yield of $CH_3O_2CH_3$ ($\phi \approx 0.007$), we can estimate the ratio k_{16}/k_{10} of the rate constants of the two competing reactions if we know the quantum yield of methanol or formaldehyde produced by the reaction (16). Dever and Calvert [16], based on their observation that $CH_3O_2CH_3$ was not detected by IR absorption in the photolysis of azomethane in the presence of oxygen, reported that this ratio may be larger than 60, while Shortridge and Heicklen [17] obtained a value of 8.9 by MS observations of peak intensities of $CH_3O_2CH_3$ and CH_3O_2H in the same system. In the present experiment the quantum yield of $CH_3O_2CH_3$ was determined by GC, but the rate of disproportionation between the two CH_3O radicals to give methanol and formaldehyde was not known. In Section 3.5 we calculated the quantum yield of formaldehyde to be 0.42, but it is necessary to consider that formaldehyde may also be formed via reaction (15) as well as via reaction (16). Therefore, the actual quantum yield of formaldehyde formed via reaction (16) may probably be less than 0.42, and the value of 0.42 may be considered to be its upper limit. In this sense we would estimate an upper limit of the ratio k_{16}/k_{10} to be 60 (= 0.42/ 0.007).

3.7. Energetic consideration of the CH_3O radical

Since the bond dissociation energy of $CH_3O—CH_3$ has been estimated to be 78 kcal mol^{-1} (326 kJ mol^{-1}) and the photon energy at 184.9 nm is

155 kcal mol^{-1} (649 kJ mol^{-1}), the excess energy of 77 kcal mol^{-1} (322 kJ mol^{-1}) must be partitioned into CH_3 and CH_3O radicals. The formation of electronically excited CH_3O is less probable since the lowest electronic excited state of CH_3O was estimated by Ohbayashi *et al.* [18] to be 94 kcal mol^{-1} (399 kJ mol^{-1}) from the emission spectra of CH_3O. Some fraction of excess energy may be kept in CH_3 or CH_3O as vibrational energy, and we may expect hot radical reactions in the low pressure experiment. Although no conclusive evidence is available in the present experiment, the increase of $\phi(CH_4)$ at low pressure (Section 3.5) may imply a reactivity enhancement of radicals (CH_3 and/or CH_3O) at low pressure.

Acknowledgement

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