Radioactive tracer of the photochemical reaction of $^{14}CS_2$ with OH in the presence of O_2*

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Abstract— The photochemical reaction of $^{14}CS_2$ with OH has been studied. The results indicated that the main products of the reaction were ^{14}COS and ^{14}CO with a small amount of $^{14}CO_2$ in the reaction system ($^{14}CS_2$-H_2O_2-C_3H_8-N_2-O_2). The reaction was promoted by oxygen. ^{14}COS and ^{14}CO had the similar kinetic curves while $^{14}CO_2$ got a different kind of curve. The overall rate constant increased with the increasing of oxygen partial pressure. The rate constant for the removal of $^{14}CS_2$ was $K = 3.4 \times 10^{-12}$ cm^3/(mol.s) at 33330 Pa O_2. The conversion of $^{14}CS_2$ to $^{14}CO_2$ at room temperature was observed and the possible mechanism of the photochemical reaction was disscussed.

Keywords: $^{14}CS_2$; OH; photochemical reaction; kinetics.

1 Introduction

Recently, it was found that the carbonyl sulfide widely distributed in the atmosphere, the concentration level is about 500 pptv. Such a large quantity of COS stable presence in the atmosphere. It pursues us to consider the sources and the path of formation of COS. The tropospheric mixing ratio reported for CS_2 indicates that its distribution is highly non-uniform and that the ratios fall off rapidly (Bandy, 1981) The tropospheric removal processes which have been proposed for CS_2 are (1) the OH initiated oxidation (Jones, 1983; Becker, 1990); (2) direct photooxidation involving the reaction of excited CS_2 with O_2 (Wine, 1981). The reaction of CS_2 with OH is an important reaction in the troposphere. Short lived reduced sulfur compounds are oxidized in the troposphere to form sulfur dioxide or be further oxidized to sulfuric

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acid. In fact the tropospheric life time of carbon disulfide is quite short (Carroll, 1985) . The rapid disappearance of CS_2 from the atmosphere indicates the existence of one or more rapid oxidation routes under natural condition. Wood (Wood, 1971) studied the photooxidation of CS_2 with radiation at 313 nm. The reaction products were CO, COS, SO_2 and polymer. But CO_2 and SO_3 were not produced. Barnes (Barnes, 1983) reported that the reaction of OH with CS_2 was rapid when O_2 presented in the photolysis mixtures. A mechanism involving the addition of OH to molecule CS_2 to form a short time lived CS_2OH adduct was discussed. As products the reaction forms one COS and one SO_2 for every reacted CS_2. Jones reported that the study of O_2 dependent rate constants for the CS_2 removal rate by OH reaction, with COS and SO_2 identified as reaction products (Jones, 1982). And the rate constant of this reaction is much higher (10^{-12} cm^3/ mol.s) in the presence of O_2. However, Iyer (Iyer, 1980) studied the reaction $^{14}CS_2$ with OH, which was produced by photolysis of H_2O_2 at 254 nm. The rate of the reaction is sufficiently slow that it is neither an important atmospheric sink for CS_2 nor an important source for atmospheric COS.

We carried out experiments on radioactive tracer to study the effects of O_2 on the reaction of OH with $^{14}CS_2$. The technique we used has the advantage that the sensitivity to impurities is unlike those encountered in flash photolysis OH disappearance measurements. Our experiments have involved the use of radioactively labeled $^{14}CS_2$, which allows the analysis of volatile products with high sensitivity by means of simple radio gas chromatographic technique (Lee, 1962) . The reaction was studied by a competitive kinetic technique in a static photolysis system in which mixtures of *CS_2, a reference propane, O_2 , N_2 and H_2O_2 were irradiated with UV light. Subsequent analysis by radio gas chromatography of the ^{14}C distribution among volatile compounds permits the measurement of ^{14}C products and the loss of $^{14}CS_2$. In general, more information about the routs of oxidation of CS_2 can be obtained.

2 Experimental part

2.1 Chemical

Radioactive $^{14}CS_2$, specific activity 55 mCi/mmol was obtained from Amersham and diluted with chromatoquality CS_2 (Matheson, Coleman and Bell) to a specific activity of 24 μ Ci/mmol. The resulting mixture contained ^{14}COS as an impurity and was purified by gas chromatography.

Hydrogen peroxide (90% FMC Corporation) was concentrated to 95% at room temperature by vacuum distillation. And stored in liquid nitrogen.

Propane, Matheson, Instrumental grade, stored in a flask linking in a vacuum

system, and degassed before use. Oxygen, Matheson, purity 99. 999%; nitrogen, Matheson, purity 99.99%.

2.2 Light source and photolysis cell

The light source is a 1000 W Xeon Mercury arc lamp operated through a Bausch & Lomb monochromator for irradiation at 320 nm and 254 nm.

A cylindrical $(15 \times 6.1 \text{ cm}^3)$ quartz photolysis cell with Superasil window was used through out the experiments. The light was focused by a quartz lens onto the entrance slit of monochromator. After pass through a quartz lens and a diaphragm, the radiation entered the front window of the photolysis cell, which contained $^{14}CS_2$ and other reactants. The transmitted radiation was measured by a RCA-935 phototube.

In order to reduce wall effect, the inner wall of the quartz photolysis cell was coated with halocarbon wax.

2.3 Analytic method for the products of photolysis reaction

After $0-4$ hours of irradiation at a given wavelength, the samples containing $^{14}CS_2$, COS, C_3H_8, CO, CO_2, O_2, N_2 were passed through a glass bead trap cooled by liquid nitrogen. The part which trapped by glass bead was called condensible fraction. The non-condensible fraction was absorbed by a silica gel loop in liquid nitrogen. The glass bead trap was connected with s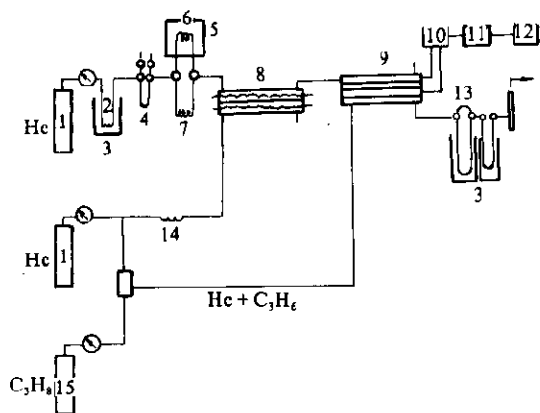ilica gel loop in series. We pay more attention to separate these two fractions as well as possible. Warmed up glass bead to room temperature, the condensible fraction was transferred from glass bead trap to a cooled injection loop. After warmed the injection loop up to room temperature, the contain of the loop was then analyzed by a radio gas chromatography equipped with TCD and a 152 cm. Chromosorb 102 column which could separate CO_2, COS, C_3H_8, and CS_2 in the order respectively. The temperature of column oven kept at 65 ℃ during chromatrographic separation of CO_2, COS, C_3H_8, while it kept at 110℃ for the separation of CS_2. The responsible coefficient of C_3H_8 was measured at each run, therefore, the recovery of C_3H_8 were determined more accurately.

Fig 1   Scheme for radiochromatographic analysis of the reaction products

1: He tank; 2: cooling finger; 3: liquid nitrogen traps;
4: injection loop; 5: column oven;
6: chromosorb 102 column; 7: charcoal column;
8: TCD cell; 9: proportional counter;
10: high voltage supply; 11: amplifier; 12: multichannel analyzer series 30; 13: glass bead traps;
14: silica gel loop; 15: propane tank

The uncondensible fraction was absorbed by silica gel loop in liquid nitrogen. The loop was connected with a 1524 cm charcoal column which can be used to separate the reaction product ^{14}CO. When the temperature of the loop raised to room temperature, the reaction products were desorbed and injected into the gas radio chromatography.

2.4   Determination of ^{14}C radioactivity

The radioactive compounds of the reaction products were determinated by a radio active chromatography equipped with a 1524cm Chromosorb 102 column, a TCD and a two layer sandwich Mylar film proportional counter. A multichannel Analyzer Series 30 was used to record the counts of each radioactive compound. The schematic diagram of the radio chromatographic analysis is shown in Fig. 1.

3   Results

3.1   The effects of O_2/CS_2 on the yield

Some experiments on the O_2 pressure dependence of the reaction of OH with CS_2 in the $^{14}CS_2$-H_2O_2-O_2-C_3H_8 system have been carried out. The effects of ratio O_2/CS_2 on the yields of the reaction products are shown in Fig. 2. When O_2/CS_2 is less than 78, the yields of all products increase fast with increasing O_2/CS_2. When O_2/CS_2 is greater than 78, the yields of the products COS and CO increase slowly. But the yields of CO_2 level off rapidly. It seems that the mechanism of formation of CO_2 is different

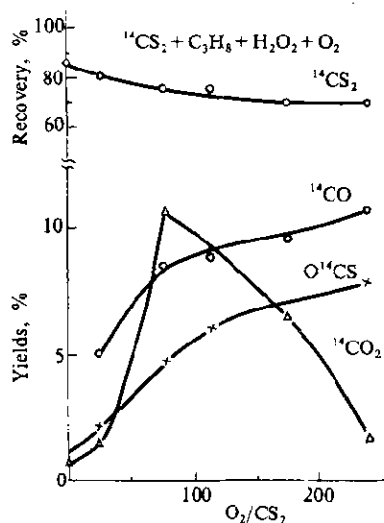Fig. 2 Effects of O_2/CS_3 on the yields of the products

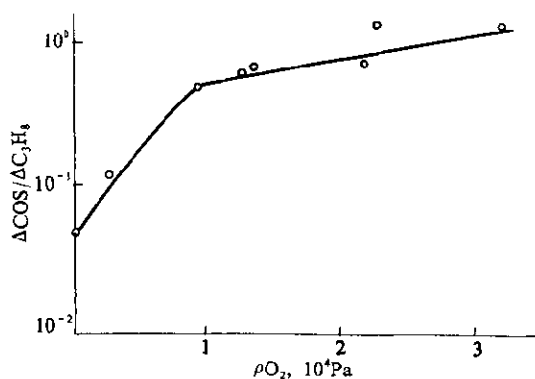Fig. 3   Relationship between lg $(\Delta^{14}COS/\Delta C_3H_8)$ and oxygen pressure

from that of COS and CO.

3.2 The effects of O_2 pressure on the effective rate constants

Investigations of the O_2 pressure dependence on the yields of the reaction in the $^{14}CS_2$-C_3H_8-H_2O_2-O_2-N_2 system have been made. The results are shown in Fig. 3. It indicates that there are two types of effects presence in these reactions. If the partial pressure of O_2 is less than 10025 Pa, the higher the partial pressure presents, the higher the yields of COS, CO and CO_2 can be obtained. Propane was selected as a reference compound in this system, and then the yields of the reaction products can be normalized by deriving-C_3H_8. The plot of $\log\{[COS]/[-C_3H_8]\}$ vs partial pressure of O_2 is shown in Fig. 3. Obviously two different slops can get from the figure. When the partial pressure of O_2 was greater than 10025 Pa, a remarkable decrease in slop was observed. On the other hand, the effect of O_2 on the yield of CO_2 is very small. It indicates that more than two kinds of paths of the effects of O_2 on the CS_2 oxidation process present. In our experiments, propane was used as a reference compound. Under steady state, if the removal of CS_2 and C_3H_8 occurs solely through reaction with OH radical, the following relationship holds:

$$\frac{\ln \dfrac{[CS_2]_t}{[CS_2]_0}}{\ln \dfrac{[C_3H_8]_t}{[C_3H_8]_0}} = \frac{K_{CS_2}}{K_{C_3H_8}} \cdot \qquad (1)$$

If $K(C_3H_8)$ is known (2.0×10^{-12}) cm^3/(mol.s), the overall rate constants of the reaction can be calculated. The rate constants were plotted vs. O_2 pressure as shown in Fig. 4. The measurement of the decrease in C_3H_8 through its reaction with OH served
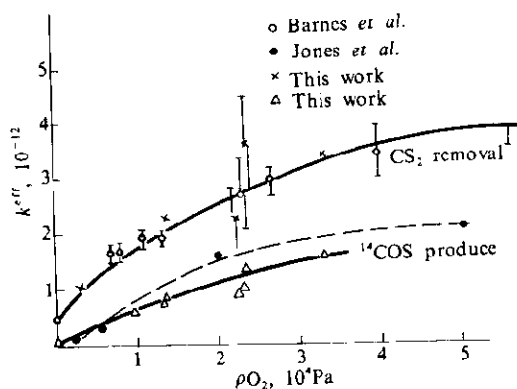

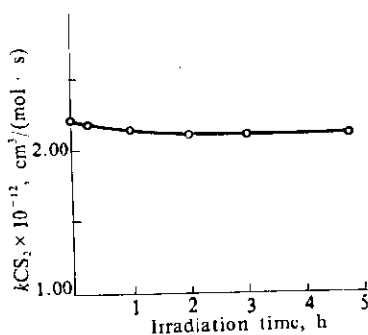Fig. 4   Effect of oxygen pressure on the rate
constant of the reaction

Fig. 5   Rate constants of the reaction at
different irradiation times

as monitor for either the removal of $^{14}CS_2$ or for the formation of ^{14}C products. The relative specific yield ($^{14}COS\%/C_3H_8\%$) of ^{14}COS increased by an order of magnitude as the pressure of O_2 was varied from 2666 Pa to 33330 Pa, the corresponding rate constants being 1.6×10^{-13} and 1.6×10^{-12} cm^3 /(mol.s), respectively.

The overall rate constant for removal of $^{14}CS_2$ was 6.7×10^{-13} cm^3 /(mol.s) at $[O_2] = 2666Pa$, and increased to 3.4×10^{-12} cm^3/(mol.s) at $[O_2] = 33330$ Pa. It is found that the results agree with the FTIR results of Barnes (Barnes, 1983).

The overall rate constant for removal of $^{14}CS_2$ at different irradiation times was shown in Fig. 5.

3.3   The formation of $^{14}CO_2$

One of the interesting results is that significant yields of $^{14}CO_2$ was observed in all over our experiments. In order to find out the possible path of the production of $^{14}CO_2$, we carried out some experiments in special cases, such as without UV irradiation or without H_2O_2 or without O_2 in the reaction system. The results are given in Table 1. From the data in Table 1, it seems that a dark reaction may take place to produce $^{14}CO_2$ in the oxidation of $^{14}CS_2$. In our experiments, the minimum detectable activity of $^{14}CO_2$ is 0.17%. However in run #604, without irradiation the yield of $^{14}CO_2$ was 0.41%. Even without O_2, as in the case of $^{14}CS_2$-H_2O_2-C_3H_8 system, 0.89% of $^{14}CO_2$ was observed. It is possible that under UV irradiation hydroperoxide may dissociate to produce O_2 and O. This may be accounted for formation of $^{14}CO_2$.

Table 1   Formation of $^{14}CO_2$ in various reaction condition

	#301	#306	#512	#514	#604	#605
$^{14}CS_2$ (Pa/133.3)	0.75	0.81	0.80	0.66	0.87	0.87
H_2O_2 (Pa/133.3)	2.60	–	2.65	–	2.67	2.69
C_3H_8 (Pa/133.3)	1.22	1.58	1.60	1.57	1.54	1.58
O_2 (Pa/133.3)	–	111.8	–	171.5	171.5	171.5
N_2 (Pa/133.3)	–	–	758.5	598.8	598.8	598.8
Total ^{14}C, Cts. × 14^{-4}	2.60	2.78	1.97	1.65	2.15	2.15
Irradiation time, h	3	3	3	3	–	3
Wavelength, nm	302	302	302	302	–	302
^{14}CO, %	6.76	5.32	0.51	0.79	ND	10.89
$^{14}CO_2$, %	0.82	1.15	0.89	0.95	0.41	2.20
^{14}COS, %	1.24	3.07	0.52	0.13	0.02	13.64
C_3H_8, %	4.24	4.97	13.25	2.24	1.65	15.84
$^{14}CS_2$, %	85.16	87.96	94.64	96.60	95.17	68.22
^{14}C recovery, %	93.98	97.50	96.56	98.47	95.60	94.95

In general, our experiments have shown that ^{14}COS and ^{14}CO are the main products of the reacting with some amount of $^{14}CO_2$. The $^{14}CO_2$ can be produced in the dark reaction. The formation of $^{14}CO_2$ is promoted by either UV irradiation or O_2 presence in the system. In the present time, the nature of the interaction between O_2 and $^{14}CS_2$ and the intermedium species also remain unspecified in this report.

3.4 The dependence of irradiation time on the yields of products

Experiments were carried out under the following conditions: $O_2/N_2 = 0.28$; irradiation wavelength, 302 nm; irradiation time, from 0 to 4.5 hours. The results are presented in Fig. 6. It is obvious that the kinetic curves of products of ^{14}COS and ^{14}CO are similar while that of $^{14}CO_2$ is different type. When the irradiation time is less than 2 hours, the plot of yields of ^{14}COS, ^{14}CO and $^{14}CO_2$ against irradiation time are all straight lines. The ^{14}COS and ^{14}CO lines pass through the origin. But the line of $^{14}CO_2$ does not pass through the origin.
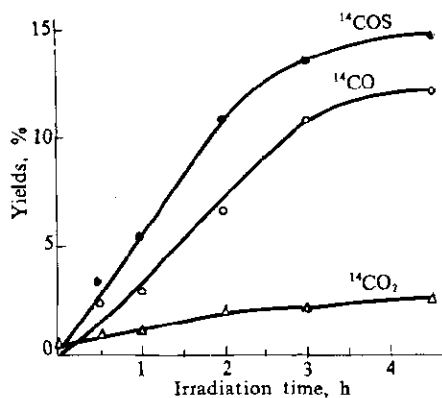
Fig. 6 Irradiation time vs. the yields of the products

3.5 The effects of irradiation wavelength on the yields of the reaction

Two sets experiments have been carried out at different irradiation wavelengths, one at 302 nm and the other at 254nm. If the wavelength was selected at 254nm; $O_2/N_2 = 0.28$; irradiation time in the range from 0 to 4.5 hours; the results are shown in Fig. 7. It is interested that the photolysis products always contain ^{14}COS, ^{14}CO and $^{14}CO_2$ when the irradiation selected either at 302 nm or at 254 nm. As the irradiation time less than one hour, the yields of ^{14}COS, ^{14}CO and $^{14}CO_2$ increase linearly with increasing irradiation time. The slop of ^{14}COS, ^{14}CO, $^{14}CO_2$ lines are 19.6, 11.2, 3.2 respectively. After one hour irradiation, the yield of ^{14}CO increases rapidly. At the termination of irradiational at 254 nm, we always observed some grey depositions on the front and rear windows of the photolysis cell. This may be results from photodissociation of carbonyl disulfide.

Fig. 7 Relationship between irradiation time and the yields of the products at $\lambda = 254nm$

4 Discussion

Recent measurements have been shown that carbonyl sulfide is widely distributed in the atmosphere. The sources and sinks of atmospheric COS are of particular interest for assessing the nature of this involvement in the stratospheric sulfur cycle. It has been suggested that CS_2 may be a precursor for atmospheric COS. Kurylo proposed that the reaction of OH with CS_2 proceeds via formation of a long lived collision complex (Kurylo, 1978).

$$OH + CS_2 \xrightarrow{K_1} [S - C - S]^* \longrightarrow products, \qquad (2)$$
$$\qquad\qquad\qquad |$$
$$\qquad\qquad\quad OH$$

$K_1 = 1.85 \times 10^{-13}$ cm^3 /(mol.s). However Rowland and Wine reported that K_1 is less than 1.5×10^{-15} cm^3 /(mol.s) (Iyer, 1980; Wine, 1980). Therefore, the reaction of OH with CS_2 can no longer be considered as the main sink route of CS_2. But the large temporal variability in CS_2 and the sharp CS_2 vertical gradient suggest that the tropospheric life time of CS_2 is short, about a week or two at most.

One possible photooxidation route of CS_2 has been proposed by Wine (Wine, 1980).

$$CS_2 \xrightarrow{\quad h\nu > 280nm \quad} CS_2^*, \tag{3}$$

$$CS_2^* + O_2 \begin{cases} \xrightarrow{\quad a \quad} CS + SOO \xrightarrow{\quad} SO_2, \\ \xrightarrow{\quad b \quad} CS_2 + O_2. \end{cases} \tag{4} \tag{5}$$
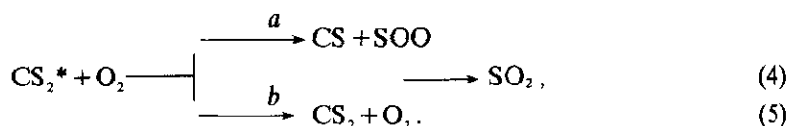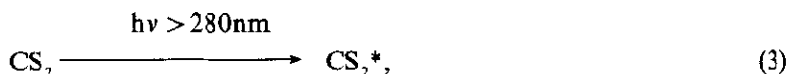
They suggested that photooxidation may be an important tropospheric sink for CS_2 and oxidation of CS_2 may be an important source of COS. In fact, in the atmosphere the reaction of OH is very important. Barnes (Barnes, 1983) reported that the overall rate constant measured for the reaction of OH with CS_2 was dependent upon the mole fraction of oxygen present in the system. The results obtained from our studies on the reaction of OH with $_{14}CS_2$ in the presence of O_2 are discussed as follows.

4.1 Oxygen effects

From the photolysis product yields measured for the reaction of CS_2 with OH, the yields increase with increasing O_2/CS_2 ranged from 0 to 78 but decrease slowly when O_2/CS_2 becomes higher. This phenomenon may be due to the fact that there are three main steps involved in the reaction. First, CS_2 is excited to CS_2^*. The second step is the addition of OH to CS_2^* to form an adduct. The third step is the reaction of O_2 with $^*CS_2OH$ and CS_2^*.

As we know, O_2 can be acted as a quencher or an oxidant. If the O_2/CS_2 is high, oxygen may act as a quencher. As a result, the concentration of CS_2^* and $^*CS_2OH$ decrease, and therefore the yields of the reaction decrease.

In case O_2/CS_2 is low, oxygen can not quench CS_2^* and / or $^*CS_2OH$. It may then react with $^*CS_2OH$ and CS_2^* to form the products.

$$*CS_2OH + O_2 \longrightarrow [*CS_2OH \ O_2]$$
$$\longrightarrow COS \qquad (6)$$
$$\longrightarrow CO.$$

Therefore, in the presence of suitable amount of O_2, the yields of reaction products are higher.

4.2 CO_2 formation and dark reaction

All of our experimental results indicate that $^{14}CO_2$ is produced in the photooxidation of $^{14}CS_2$. The formation of $^{14}CO_2$ may be from two possible routes.

First, by secondary reactions:

$$^{14}CS_2* \longrightarrow {}^{14}COS$$
$$\downarrow \qquad\qquad OH$$
$$\longrightarrow [O\text{-}C\text{-}S] \longrightarrow {}^{14}CO_2 + HS. \qquad (7)$$

If it is true, then most part of $^{14}CO_2$ is produced from ^{14}COS and the ratio of $CO/ (CO_2 + COS)$ should be constant during the reaction. In fact, the ratio of $CO/ (CO_2 + COS)$ was found to be almost constant, if the reaction time was less than 2 hour. The results are given in Table 2.

Second by dark reaction:

Our experiments showed that small amount of $^{14}CO_2$ were formed when the reactants ($^{14}CS_2$-C_3H_8-H_2O_2-O_2-N_2) were induced into the quartz photolysis cell and kept in dark for 2 or 3 hours at room temperature. It is obvious that a dark reaction takes place in the system, but the mechanism of it remains unknown. In order to distinguish the dark reaction from other reaction we use the following expression.

$$^{14}CS_2* + O_2 \longrightarrow \longrightarrow {}^{14}CO_2. \qquad (8)$$

4.2 Reaction mechanism

Based on the above discussion, we propose the following mechanism for the reaction studied.

In the system, three kinds of reaction may take place.

4.2.1 Photo oxidation

In the first step, carbon disulfide molecule is excited by irradiation; then the excited CS_2* reacts with OH radical and / or O_2 to form a series of products. In other case, excited CS_2* may be quenched by O_2 and converted back to CS_2. The reactions are expressed as follows.

Table 2   The ratio of $CO / (CO + COS)$

	#601	#602	#603	#605	#606
^{14}CO, %	2.94	2.42	6.64	10.89	12.24
$^{14}CO_2 + {}^{14}COS$, %	6.27	4.04	12.90	15.84	17.50
$^{14}CO / ({}^{14}CO_2 + {}^{14}COS)$	0.47	0.60	0.51	0.69	0.70

$$CS_2 + h\gamma \longrightarrow CS_2{}^*, \tag{9}$$

$$CS_2{}^* + OH \longrightarrow [CS_2OH]^*, \tag{10}$$

$$[CS_2OH]^* + O_2 \longrightarrow [CS_2OHO_2]^*, \tag{11}$$
$$\longrightarrow COS$$
$$\longrightarrow CO$$

$$CS_2{}^* + O_2 \longrightarrow CS + S - OO$$
$$\longrightarrow SO_2, \tag{12}$$

$$CS + O_2 \longrightarrow COS + O$$
$$| \tag{13}$$
$$\longrightarrow CO + SO,$$

$$CS_2{}^* + O_2 \xrightarrow{\quad quench \quad} CS_2 + O_2. \tag{14}$$

4.2.2   Secondary reaction

Because of using only ^{14}C as the labeled atom in our studies, the discussion here is limited on the secondary reaction of carbon atom only. The formation of $^{14}CO_2$ may results from the following secondary reactions.

$$COS + OH \longrightarrow [O - C - S] \longrightarrow CO_2 + HS, \tag{15}$$
$$|$$
$$OH$$

$$CO + OH \longrightarrow [HOCO] \longrightarrow CO_2 + H. \tag{16}$$

Experimental results showed that CO_2 is mainly formed from the reaction of COS with OH.

4.2.3   Dark reaction

It seems that a dark reaction also takes place in this system. The reaction mechanism remains to be investigated in the future.

5 Conclusion

With O_2 and N_2 as diluent gases and one atmosphere total pressure, rapid removal of $^{14}CS_2$ was observed when H_2O_2 was present in the irradiation mixture. The main products were COS and CO. The overall rate constant for the removal of $^{14}CS_2$ was determined to be 6.7×10^{-13} cm^3 /(mol.s) at $O_2 = 2666$ Pa, and increasing to 3.4×10^{-12} cm^3/(mol.s) at $O_2 = 33330$ Pa. Therefore the reaction of OH with CS_2 in the presence of O_2 may be considered as important route of CS_2 sink in the atmosphere.

$^{14}CO_2$ was detected in all of our photochemical experiments. Even in dark reaction, a few amount of $^{14}CO_2$ can be determined, at the same experiments ^{14}COS and ^{14}CO can not be detected any more. We proposed that CS_2 can be oxidated to form CO_2 in dark at room temperature.

The possible reaction mechanism is discussed. Three kinds of reaction may take place in the system studied; these are photooxidation reaction, secondary reaction and dark reaction.

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