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THE PHOTOOXIDATION OF CS_2 AT 2139 Å

WILLIAM P. WOOD* and JULIAN HEICKLEN

Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pa. 16802 (U.S.A.)

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SUMMARY

The photooxidation of CS_2 was studied at 2139 Å and 25°C. The products of the reaction are CO, OCS, SO_2, and S_2O. Possibly SO_3 is also produced, though we have no positive evidence for it. CO_2 is not a product.

As the reaction products accumulate in any run, the reaction is inhibited and the ratio $\Phi\{OCS\}/\Phi\{CO\}$ is enhanced. Both effects are attributed to the terminating reaction:

$$CS + S_2O \rightarrow OCS + S_2$$

This reaction would compete with the predominant reactions producing CO and OCS, *i.e.*:

$$CS + O_2 \rightarrow CO + SO$$

$$\rightarrow OCS + O$$

The primary photochemical process produces excited CS_2 molecules which can decompose to CS + $S(^3P)$ or be quenched by O_2 and CS_2. The sulfur atom reacts with either O_2 or CS_2. Otherwise the mechanism is essentially the same as at 3130 Å in the early stages of the photooxidation, except at high O_2 pressures and absorbed intensities. Under these conditions additional reactions are needed to produce OCS, one of which is:

$$CS + SO \rightarrow OCS + S$$

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* Present address: Department of Applied Science, Building 815, Brookhaven National Laboratory, Upton, L.I., N.Y. 11973 (U.S.A.)

INTRODUCTION

The oxidation of CS_2 has been the subject of comprehensive study in our laboratory[1-4] because, during the oxidation, CS and SO are produced as intermediates in the reaction. These species are also known to be unstable intermediates in the oxidation of other atmospheric pollutants such as H_2S, OCS, and various organic compounds[5]. An understanding of the CS_2 oxidation should shed light upon the reactive mechanisms operative in these other systems. SO and CS once produced would be expected to undergo oxidation irrespective of their source of production.

In our previous study[1,3] of the photooxidation at 3130 Å, there was insufficient energy to dissociate CS_2. In the present study, carried out at 2139 Å, photodissociation can occur, and additional reactions are needed. Furthermore, since the product quantum yields are so much greater than at 3130 Å, S_2O production can be monitored and its influence on the reaction examined.

EXPERIMENTAL

The gases used were obtained from the Matheson Company. These included extra dry grade O_2 which contained 300 ppm of N_2. For purposes of calibration C.P. grade CO, commercial grade CO_2, anhydrous SO_2, and C.P. grade OCS were used without further purification except degassing at −196°C for the last three gases. The C.P. grade CO contained about 2% air. The commerical grade CO_2 showed one unidentified impurity (~3 %). The anhydrous SO_2 showed no impurities, while the OCS contained about 3% CO_2 and much smaller amounts of H_2S. The HBr which was used for actinometric studies was first degassed at −196°C to remove any H_2 impurity and then distilled from −130°C into −196°C to remove any Br_2 impurity. Fisher Scientific Company spectral grade CS_2 was used after degassing at −196°C. No impurities ($<$ 10 ppm) were found.

Pressures less than 10 Torr were measured on a McLoud gauge. For pressures in the range 10–50 Torr a Wallace–Tiernan absolute pressure indicator was used. A mercury manometer in conjunction with a cathetometer was used to measure pressures greater than 50 Torr.

The photolytic assembly consisted of a cylindrical quartz cell, 10 cm in length and 5 cm in diameter, which was used as the reaction vessel. The cell was attached to the vacuum system by a graded quartz-to-Pyrex seal and a Teflon stopcock. The photolytic lamp, a Philips 93106E spectral Zn lamp (2139 Å), was mounted on an optical bench which was positioned perpendicular to the longitudinal axis of the reaction cell. The incident radiation passed through a 5 cm long quartz cell containing chlorine before entering the side of the reaction vessel. The chlorine filter removed any incident radiation in the wavelength range 2800–4000 Å. The effective radiation was at 2139 Å.

The reaction was monitored continuously by ultra-violet absorption spectroscopy using low intensities so that photochemical reactions were not induced by the monitoring lamp. The monitoring source was an Osram 150 W high pressure xenon lamp, which emits continuous radiation from 2000 Å to the infra-red region. The light is focused by two quartz lenses onto the entrance slit of a Jarrell-Ash 82-410 0.25 m Ebert monochromator with 500 μm slits and an 1180 groove/mm grating blazed at 3000 Å. The monochromator was calibrated with the line spectrum of a medium-pressure Hanovia mercury lamp. After passing through the windows of the reaction cell, the radiation was focused by another quartz lens onto a RCA 9–35 phototube and the response registered on a Texas Instruments 1 mV recorder.

Actinometry was accomplished by photolyzing HBr and measuring the H_2 produced. The quantum yield for H_2 production is 1.0[6]. The technique of matched absorbances between the HBr and CS_2 at 2139 Å was employed to eliminate any geometrical corrections. In order to accomplish this matching, the extinction coefficients (to base 10) of both HBr and CS_2 at 2139 Å were measured; they were, respectively, 5.34×10^{-3} Torr^{-1} cm^{-1} and 4.70×10^{-2} Torr^{-1} cm^{-1}.

In each experiment, after the reaction was terminated, the products were collected and analyzed by gas chromatography. The gases that were non-condensable at $-196°$C were collected with a Toepler pump and passed through a 15 ft., 5 Å molecular sieve column operating at 50° C and a He flow rate of 150 cm^3/min. The condensable gases were collected and analyzed on a 10 ft. Porapak Q column at 70° C with a He flow rate of 250 cm^3/min. In both cases a Gow Mac Model 40-050 voltage regulator with a thermistor detector was used in conjunction with a 1 mV recorder.

RESULTS

Eighty minute irradiations were carried out initially, the characteristic absorption spectrum of S_2O was seen[7], and the S_2O optical absorption at 2960 Å was monitored. SO_2, CO, and OCS were measured by gas chromatography at the end of the irradiation. CO_2 was not produced. SO_3 was not found and thus was not a major product, but our analytical scheme would not have detected small amounts[3].

A typical time plot of $[S_2O]$ is shown in Fig. 1. The optical density at 2960 Å was converted to S_2O pressures using the extinction coefficient of 0.163 cm^{-1} Torr^{-1} found by Cehelnik[7]. S_2O is an initial product, but its rate of production falls as the reaction proceeds. A number of runs for the same reaction conditions, *i.e.* 8.0 Torr of CS_2 and 40 Torr of O_2, were carried out for various irradiation times and the average quantum yields of OCS and CO were measured. They are listed in Table 1. Both $\Phi\{OCS\}$ and $\Phi\{CO\}$ decrease as the irradiation time is lengthened. Furthermore the ratio $\Phi\{OCS\}/\Phi\{CO\}$ increases with irradiation time.

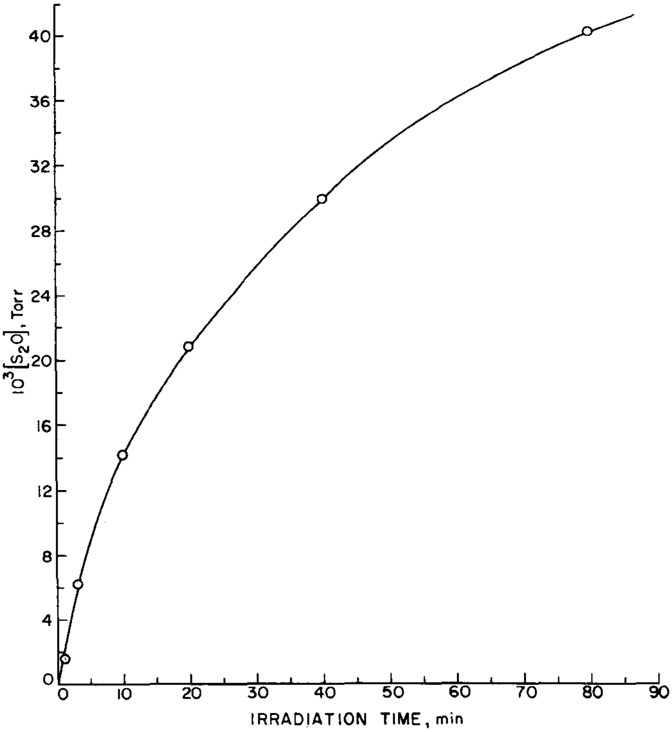

Fig. 1. S_2O production in the photooxidation of CS_2 at 2139 Å, 25°C, $I_a = 3.36$ mTorr/min, $[CS_2] = 8.0$ Torr, and $[O_2] = 40.1$ Torr.

It is clear that one or more of the products enters into secondary reactions causing inhibition. The reaction we consider most likely is:

$$CS + S_2O \rightarrow OCS + SO$$

Not only does this reaction remove S_2O, but it reduces the importance of the chain oxidation steps involving CS, since SO produces SO_2 most of the time in a

TABLE 1

EFFECT OF IRRADIATION TIME ON THE PHOTOOXIDATION OF CS_2 AT 2139 Å[a]

Irradiation time (min)	[OCS] (mTorr)	[CO] (mTorr)	$[S_2O]$ (mTorr)	$\Phi\{OCS\}$	$\Phi\{CO\}$	$\frac{\Phi\{OCS\}}{\Phi\{CO\}}$	$\Phi\{S_2O\}$
1.00	12.2	7.65	—	3.47	2.18	1.60	—
5.00	42.6	19.2	—	2.43	1.09	2.12	—
10.00	65.0	20.4	—	1.85	0.58	3.18	—
40.00	210	62.5	32	1.49	0.445	3.37	0.23
94.00	434	117	43.5	1.31	0.35	3.70	0.123

[a] $[CS_2] = 8.1 \pm 0.1$ Torr; $[O_2] = 41 \pm 1$ Torr; $I_a = 3.52$ mTorr/min.

non-chain step. Thus the oxidation is inhibited as S_2O accumulates. Furthermore the above reaction is an additional source of OCS, but not CO, so that $\Phi\{OCS\}/\Phi\{CO\}$ increases with irradiation time.

In addition to the above complication, the runs were irreproducible. As the cell became more and more conditioned, the quantum yields fell, and ultimately reproducibility was attainable. This effect was also noticed in our earlier studies[1-4]. All subsequent runs were performed in the conditioned cell for very short conversions to eliminate secondary reactions. Under these conditions, insufficient S_2O was produced to measure quantitatively. Since S_2O decomposes in part to SO_2, SO_2 analysis would not be particularly meaningful; SO_2 was not measured either. Thus quantum yields for only OCS and CO were obtained in the subsequent short irradiation runs; these are believed to be true initial quantum yields.

Experiments were made at CS_2 pressures of about 72, 8.0, 2.1, 1.0, and 0.5 Torr at full intensity and reduced intensity. The O_2 pressure was varied from 760 to 0.8 Torr. The results are listed in Table 2.

TABLE 2

INITIAL QUANTUM YIELDS IN THE PHOTOLYSIS OF CS_2–O_2 MIXTURES AT 2139 Å AND 25°C

$[O_2]/[CS_2]$	$[O_2]$ (Torr)	$[CS_2]$ (Torr)	$10^3 I_a$ (Torr/min)	$\Phi\{CO\}$	$\Phi\{OCS\}$	$\Phi\{OCS\}/\Phi\{CO\}$
$[CS_2]$ = 70–75 Torr, irradiation time = 2.00 min						
9.45	711	75.0	4.65	0.65	2.65	4.07
5.10	363	71.0	6.05	0.68	1.93	2.84
4.19	310	74.0	4.65	0.75	1.59	2.12
0.97	69.0	71.0	6.05	0.65	0.92	1.41
0.22	15.0	70.0	6.05	0.40	—	—
0.10	7.0	70.0	6.20	0.13	0.14	1.08
$[CS_2]$ = 8.0–8.1 Torr, irradiation time = 2.00 min						
95.0	760	8.0	4.50	0.43	1.20	2.80
63.4	506	8.0	4.50	0.55	1.32	2.40
50.2	406	8.1	4.50	0.77	1.85	2.40
40.8	327	8.0	4.50	0.76	1.60	2.11
9.25	74.0	8.0	4.50	1.08	1.71	1.58
7.5	60.0	8.0	4.50	1.15	1.80	1.56
6.25	50.0	8.0	4.50	1.12	1.79	1.59
3.14	25.5	8.1	4.50	1.13	1.47	1.30
1.98	15.9	8.0	4.50	1.08	1.48	1.37
1.27	10.3	8.1	7.35	0.88	—	—
0.60	4.8	8.0	4.50	0.81	1.09	1.34
0.10	0.80	8.0	7.35	0.35	—	—
$[CS_2]$ = 2.0–2.3 Torr, irradiation time = 2.00 min						
217	435	2.0	2.26	0.58	1.67	2.88
198	416	2.1	3.12	0.44	1.06	2.40
195[a]	410	2.1	0.30	0.45	0.81	1.80
163	341	2.1	3.65	0.44	1.10	2.52
107	215	2.0	2.26	0.90	1.61	1.79
106	223	2.1	4.20	0.70	—	—
52.5[a]	105	2.1	0.30	1.16	—	—

Table 2 cont.

$[O_2]/[CS_2]$	$[O_2]$ (Torr)	$[CS_2]$ (Torr)	$10^3 I_a$ (Torr/min)	$\Phi\{CO\}$	$\Phi\{OCS\}$	$\frac{\Phi\{OCS\}}{\Phi\{CO\}}$
44.5	103	2.3	2.12	1.25	2.04	1.63
24.5	49.0	2.0	2.32	1.32	1.57	1.19
12.3	24.7	2.0	2.26	1.42	1.75	1.23
5.8	11.6	2.0	4.80	1.55	1.93	1.26
5.4	10.7	2.0	3.89	1.64	1.83	1.12
5.2	10.4	2.0	3.89	1.57	–	–
5.1	10.2	2.0	4.80	1.60	1.68	1.05
4.9	9.8	2.0	3.89	1.59	1.85	1.16
4.6	9.3	2.0	3.89	1.63	2.02	1.24
$[CS_2]$ = 0.90–1.10 Torr, irradiation time = 2.00 min						
332	309	0.93	1.95	0.36	0.79	2.20
207	207	1.01	1.95	0.68	1.73	2.55
206	206	1.00	1.42	0.61	1.52	2.00
190[a]	209	1.10	0.184	0.83	1.28	1.64
160[a]	160	1.00	0.184	0.77	1.28	1.44
114	103	0.90	1.42	0.91	1.91	2.10
103[a]	103	1.00	0.184	1.32	1.42	1.08
102	101	0.99	1.95	1.10	2.32	2.11
75.5	83.0	1.10	1.95	1.32	2.31	1.75
51.0	49.0	0.96	2.10	1.38	2.05	1.48
37.6	34.6	0.92	2.10	1.45	1.98	1.37
16.6	16.8	1.01	2.10	1.66	2.16	1.30
4.05	4.05	1.00	2.02	1.74	2.14	1.23
3.59	3.40	0.95	2.02	1.75	2.07	1.18
$[CS_2]$ = 0.48–0.58 Torr, irradiation time = 2.00 min						
1400[b]	690	0.49	1.01	–	0.45	–
563[b]	326	0.58	1.01	0.32	0.84	2.63
406	204	0.50	1.01	0.48	1.36	2.83
267	147	0.55	1.01	0.85	1.87	2.20
236[a]	127	0.54	0.109	1.05	1.16	1.10
200	105	0.53	1.01	1.10	2.95	2.68
100	55.0	0.55	1.01	1.40	2.75	1.97
93.0[a]	48.5	0.52	0.109	1.41	1.65	1.17
24.4	12.2	0.50	1.01	1.70	2.30	1.35
9.1	5.0	0.55	1.01	1.88	2.22	1.18
6.0	2.85	0.48	1.01	2.02	2.54	1.26

[a] Irradiation time = 20.0 min.

[b] Irradiation time = 10.0 min.

At any CS_2 pressure, the observed quantum yield of CO formation, $\Phi\{CO\}$, increases with the $[O_2]/[CS_2]$ ratio, passes through a maximum at $[O_2]/[CS_2] \sim 10$, and then decreases with further increases in $[O_2]/[CS_2]$. For a given $[O_2]/[CS_2]$ ratio, $\Phi\{CO\}$ increases as $[CS_2]$ drops. These results are depicted in Fig. 2.

The ratio $\Phi\{OCS\}/\Phi\{CO\}$ is about 1.3 ± 0.2 at low O_2 pressures, but increases noticeably with the O_2 pressure. For runs at similar reactant pressures but different absorbed intensities, I_a, the ratio $\Phi\{OCS\}/\Phi\{CO\}$ is larger at higher I_a.

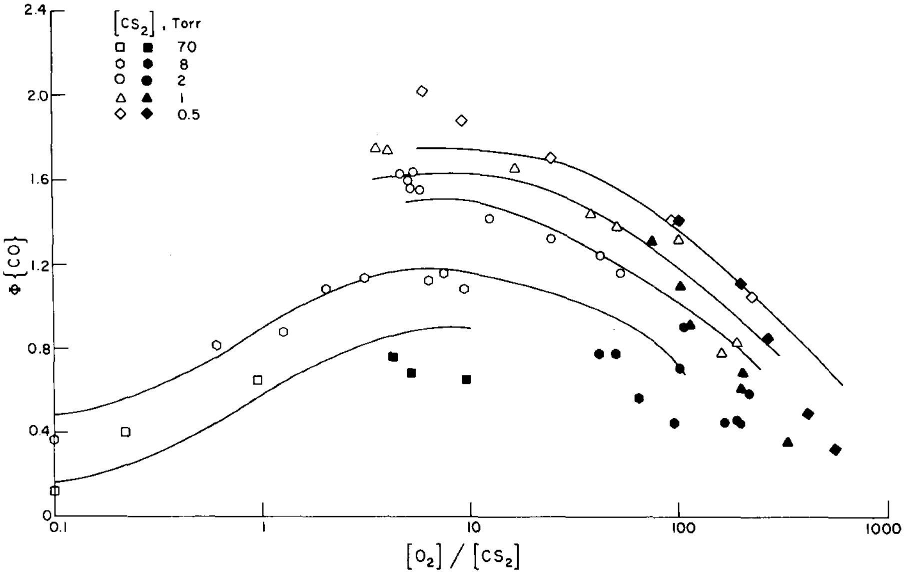

Fig. 2. Semi-log plots of $\Phi\{CO\}$ *vs.* $[O_2]/[CS_2]$ in the photooxidation of CS_2 at 2139 Å and 25°C. Open symbols: $\Phi\{OCS\}/\Phi\{CO\} < 1.65$; solid symbols: $\Phi\{OCS\}/\Phi\{CO\} > 1.65$. Solid lines are theoretically computed curves from the mechanism using the rate constant ratios in Table 3.

DISCUSSION

The mechanism for the photooxidation of CS_2 at 3130 Å has been presented previously[3]. With modifications to allow for the additional energy at 2139 Å, this mechanism is:

$$CS_2 + h\nu \rightarrow CS_2^* \tag{1}$$

$$CS_2^* \rightarrow CS + S \tag{2}$$

$$CS_2^* + O_2 \rightarrow CS + SO_2^* \tag{3a}$$

$$CS_2^* + O_2 \rightarrow CS_2 + O_2 \tag{3b}$$

$$SO_2^* \rightarrow SO + O \tag{4}$$

$$SO_2^* + M \rightarrow SO_2 + M \tag{5}$$

$$CS_2^* + CS_2 \rightarrow 2CS + S_2 \tag{6a}$$

$$\rightarrow 2CS_2 \tag{6b}$$

$$S + O_2 \rightarrow SO + O \tag{7}$$

$$S + CS_2 \rightarrow CS + S_2 \tag{8}$$

$$CS + O_2 \rightarrow CO + SO \tag{9a}$$

$$\rightarrow OCS + O \tag{9b}$$

$$O + CS_2 \rightarrow CS + SO \tag{10}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{11}$$

where CS_2^* is the photoexcited state of CS_2, and SO_2^* is a highly energized form of SO_2 (probably SOO). The SO ultimately produces SO_2 and S_2O in terminating steps. The termination occurs mainly on the wall of the reaction vessel, but reaction of SO with O_3 to produce SO_2 or with O_2 to produce SO_3 might also play a role.

The major modification in the mechanism is the production of $S(^3P)$ by reaction (2), since the absorption of radiation below 2200 Å is known to produce $S(^3P)$ by photodissociation[8]. At 3130 Å, there is insufficient energy for reaction (2) to occur. The sulfur atoms can then be removed by the well established reaction 7[9]. There is no evidence concerning sulfur atom removal by CS_2 (reaction 8) but we have included it for generality.

Another difference in the mechanism above and that proposed for photolysis at 3130 Å concerns the fate of SO_2^*. At 3130 Å, SO_2^* always reverts to SO_2, but because of the additional energy at 2139 Å, the possibility exists that SO_2^* can dissociate at the shorter wavelength.

The mechanism predicts that:

$$\Phi\{OCS\}/\Phi\{CO\} = k_{9b}/k_{9a} \tag{I}$$

In previous work[3,4], k_{9b}/k_{9a} was found to be 1.2. The ratio $\Phi\{OCS\}/\Phi\{CO\}$ is tabulated for each run in Table 2. For most of the runs, the ratio is between 1.0 and 1.5. However, for many runs at high O_2 pressures, the ratio is considerably higher. Clearly under these conditions an additional reaction which produces OCS is needed. However, for the time being, let us ignore these runs and consider only those runs with $\Phi\{OCS\}/\Phi\{CO\} < 1.65$. Then $\Phi\{CO\}$ is:

$$\frac{\begin{array}{c}[2k_2 + (1+\beta)k_{3a}[O_2] + 2k_{6a}[CS_2] + \\ (k_{11}[O_2][M]/k_{10}[CS_2])(k_2 + k_{3a}[O_2] + 2k_{6a}[CS_2] + \alpha k_2)]\end{array}}{(1 + k_9 k_{11}\,[O_2][M]/k_{9a}k_{10}[CS_2])(k_2 + k_3[O_2] + k_6[CS_2])} \tag{II}$$

where $k_3 \equiv k_{3a} + k_{3b}$, $k_6 \equiv k_{6a} + k_{6b}$, $k_9 \equiv k_{9a} + k_{9b}$,

$\alpha \equiv k_8[CS_2]/(k_7[O_2] + k_8[CS_2])$

$\beta \equiv k_4/(k_4 + k_5[M])$

Equation (II) is quite complex, but numerous simplifications can be made. At high CS_2 pressures, $\Phi\{CO\}$ drops considerably so that the quenching of CS_2^* by CS_2 must be primarily by reaction (6b), and reaction (6a) can be neglected. However, increasing the O_2 pressure for $[O_2]/[CS_2] < 10$ increases $\Phi\{CO\}$, so that quenching of CS_2^* by O_2 must be primarily by reaction (3a), and reaction (3b) can be neglected. Also the term involving α is only important when reaction (10) is of comparable importance to reaction (11), *i.e.* at high values of $[O_2]/[CS_2]$. However, under these conditions $\alpha \sim 0$. Thus eqn. (II) can be reduced to:

$$\Phi\{CO\} = \frac{2 + (1+\beta)k_{3a}[O_2]/k_2 + (k_{11}[O_2][M]/k_{10}[CS_2])(1 + k_{3a}[O_2]/k_2)}{(1 + k_9k_{11}[O_2][M]/k_{9a}k_{10}[CS_2])(1 + k_{3a}[O_2]/k_2 + k_{6b}[CS_2]/k_2)} \tag{III}$$

The relative quenching efficiency of CS_2 and O_2 probably lies between 1 and 5 for both reactions (5) and (11). For our experimental conditions, detailed calculations show that eqn. (III) is very insensitive to the relative efficiency of the quenching gases if CS_2 is $\leqslant 5$ times as efficient as O_2. For convenience we set $[M] = [O_2] + 3[CS_2]$.

The right-hand side of eqn. (III) depends on 5 rate constant ratios: k_{3a}/k_2, k_{6b}/k_2, k_5/k_4, k_9/k_{9a}, and k_{11}/k_{10}. The ratio k_9/k_{9a} is known from our previous work to be 2.2[3,4]. At 25°C the rate constant k_{11} is $2.5 \times 10^8\ M^{-1}\ s^{-1}$ [10], whereas that for reaction (10) is $2.5 \times 10^9\ M^{-1}\ s^{-1}$ [11–13]. Thus $k_{11}/k_{10} = 5.4 \times 10^{-6}$ Torr^{-1}. The other three rate constant ratios were computer fitted to the experiments in which $\Phi\{OCS\}/\Phi\{CO\} \leqslant 1.65$. The values used are listed in Table 3. The curves for $\Phi\{CO\}$ computed from these ratios and eqn. (III) are plotted in Fig. 2, and they fit the data points reasonably well.

The experimental values for $\Phi\{CO\}$ for runs in which $\Phi\{OCS\}/\Phi\{CO\} > 1.65$ are all lower than expected from the curves computed from eqn. (III). Thus for these runs additional reactions must be occurring which produce OCS at the expense of CO. Furthermore, for runs with similar reactant pressures, but different I_a, $\Phi\{OCS\}/\Phi\{CO\}$ is larger at the higher I_a. Consequently the reactions involved must be between CS and some other unstable intermediate in the system. The possibilities are:

$$CS + SO_2^* \rightarrow OCS + SO$$
$$CS + O_3 \rightarrow OCS + O_2$$
$$CS + S_2O \rightarrow OCS + S_2$$
$$CS + SO_3 \rightarrow OCS + SO_2$$
$$CS + SO \rightarrow OCS + S$$

The first four of these reactions are chain-terminating steps. Since they compete with the chain propagating step, reaction (9b), they should tend to reduce $\Phi\{CO\} + \Phi\{OCS\}$. In fact, when $\Phi\{OCS\}/\Phi\{CO\}$ is enhanced, so is $\Phi\{OCS\} + \Phi\{CO\}$. Consequently, the last reaction, which is a chain propagating reaction,

TABLE 3

RATE CONSTANT RATIOS

Ratio	Value	Units
k_{3a}/k_2	0.6	Torr^{-1}
k_{3b}/k_2	0	Torr^{-1}
k_{6a}/k_2	0	Torr^{-1}
k_{6b}/k_2	0.6	Torr^{-1}
k_5/k_4	0.026	Torr^{-1}
k_{9b}/k_{9a}	1.2[a]	none
k_{11}/k_{10}	5.4×10^{-6} [a]	Torr^{-1}

[a] These ratios set to conform to known rate constants.

must play some role. However, if it were the sole additional reaction, $\Phi\{CO\}$ would remain unchanged as $\Phi\{OCS\}$ was increased. Since, in fact, $\Phi\{CO\}$ apparently drops as $\Phi\{OCS\}$ is enhanced, one or more of the first four reactions is probably also playing some role.

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