ments the O_3 uv band disappeared gradually as the temperature was raised, whereas the ir bands disappeared quickly over a small temperature range. Furthermore, if the ratio of the ir and uv extinction coefficients for O_3 are the same in the vapor phase and when condensed at −185°, then the 2100- and 1030-cm^{-1} bands were too intense by a factor of 10 to be condensed O_3.

If the above species is a complex it could be either a π or σ complex. The possibility of such complexes has been suggested by several workers.[1,38,43,44] Evidence for a π complex from 1-mesityl-1-phenylethylene and other mesityl compounds has been given very recently by Bailey, *et al.*[43]

The considerable speculation as to the number of species involved in the transformation of olefin to high-temperature products by reaction with ozone[1,37,38] must be tempered by the existence of a single primary ozonide at temperatures above −175°. The implications suggest that any new species to be invoked must either be transitory on the way to products from the primary ozonide (such as the zwitterion **2** or the Staudinger molozonide **7**) or be transitory on the way to primary ozonide at −175° (such as a π complex).

Conclusion

The reaction of ozone with simple olefins and the subsequent product transformations can be followed in the ir in the temperature range −175 to −80°. The results indicate the possibility of a π complex and the formation of one primary ozonide characterized by strong bands around 1000 and 700 cm^{-1}. The primary ozonide decomposes to yield the normal ozonolysis products observed at higher temperatures.

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Photolysis of Sulfur Dioxide in the Presence of Foreign Gases. II. Thiophene

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Abstract: The SO_2 photosensitized decomposition of thiophene vapor was studied at 25 ± 3° with irradiation from a mercury arc (effective λ = 3130, 3022, and 2967 Å). Two types of products were formed. Type I products are those produced in the direct photolysis of thiophene, *i.e.*, C_2H_2, CH_2CCH_2, CH_3CCH, CS_2, CH_2CHCCH, and polymer. Type II products are H_2 (the major product), CH_2CO, and SCO. Traces of C_2H_4 and C_3H_6 were also found. Experiments with NO, which quenches the triplet states of SO_2, and with N_2, which quenches the emitting singlet state of SO_2, as well as experiments in which the triplet emitting state $^3SO_2$ was directly produced by radiation >3600 Å established that $^3SO_2$ was not the sensitizing state, that type I products came from sensitization of SO_2^* and SO_2^{**} (the nonemitting singlet and triplet states of SO_2, respectively), and that type II products came mainly, if not entirely, from sensitization by $^1SO_2$ (the emitting singlet state) and SO_2^*. A simplified mechanism is presented which adequately explains the results, and a number of rate constant ratios are obtained.

The interest in the mechanism of the reactions between electronically excited SO_2 and different added gases has increased in the last years mainly because of the general concern about the nature of the chemical processes taking place in SO_2 polluted atmospheres. Since the ozone present in the atmosphere absorbs the radiation lying in the 2000–3000 Å region, the wavelengths of interest are those larger than 2900 Å which correspond to energies lower than 99 kcal/mol. Thus, under atmospheric conditions, the high OS–O bond dissociation energy (132 kcal/mol at 298°K) precludes its direct photodecomposition. Hence, the reactions of atmospheric importance are those of electronically excited SO_2, principally when excited into the first singlet band, centered at 2900 Å.

The mechanism for the primary photophysical processes in SO_2 when excited into this band is

$$SO_2 + h\nu \longrightarrow {}^1SO_2 \tag{I_a}$$

$$^1SO_2 + SO_2 \longrightarrow 2SO_2 \tag{1a}$$

$$\longrightarrow {}^3SO_2 + SO_2 \tag{1b}$$

$$^1SO_2 \longrightarrow SO_2 + h\nu_f \tag{2a}$$

$$\longrightarrow SO_2 \tag{2b}$$

$$\longrightarrow {}^3SO_2 \tag{2c}$$

$$^3SO_2 \longrightarrow SO_2 + h\nu_p \tag{3a}$$

$$\longrightarrow SO_2 \tag{3b}$$

$$^3SO_2 + SO_2 \longrightarrow 2SO_2 \tag{4a}$$

$$\longrightarrow SO_3 + SO \tag{4b}$$

The details of this mechanism have been elucidated by several workers through emission studies using direct and sensitized excitation.[1-12] The rate constants have been calculated for all the steps. The results obtained during the study of the reactions between SO and O_3 are consistent with the above mechanism.[13-18] The photochemical reaction between SO_2 and O_2 has been the object of several studies, but the mechanism for the production of SO_3 is still not well understood.[19,20] The reactions of excited SO_2 with CO and excited SO_2 with hydrocarbons have been the object of several studies which include those from Dainton and Ivin,[21,22] Timmons,[23] and Calvert and coworkers.[24-26] The Calvert group studied the SO_2–CO system when SO_2 was directly excited to $^3SO_2$ and found that CO_2 was produced in a manner consistent with the above mechanism.

The studies of the photochemical interaction of SO_2 with CO and SO_2 with C_2F_4 using 3130-Å radiation were performed in our laboratory.[27] In both cases, the product quantum yields were independent of the SO_2 pressure at high SO_2 pressures, a result not expected from the above mechanism. The same result was found in the SO_2–hydrocarbon systems by Dainton and Ivin.[22]

The addition of excess N_2, a known[6] quencher of $^1SO_2$, had no effect in the SO_2–C_2F_4 system. The same addition reduced $\Phi\{CO_2\}$ about 60% at low CO and SO_2 pressures but had no effect at large CO pressures in the SO_2–CO system. These results agree with those of Timmons[23] who found that the addition of CH_4, another good quencher of singlet SO_2 molecules, did not affect product formation. In both cases (SO_2–CO, SO_2–C_2F_4), the addition of NO inhibited but did not eliminate product formation.

The results were interpreted in terms of a more complex mechanism in which the chemically reactive species (a singlet and a triplet) were different from those responsible for the emitting processes. The mechanism proposed was consistent with the emission and the other photochemical studies.

In order to further elucidate the mechanism of the photochemical reactions of electronically excited SO_2, we have studied the system SO_2–thiophene. The photochemistry of thiophene itself was elucidated in our laboratory recently.[28] Thiophene vapor was photoexcited with 2139 and 2288 Å radiation, as well as by mercury sensitization at 2537 Å. In all cases the products were C_2H_2, CH_2CCH_2, CH_3CCH, CS_2, CH_2CHCCH, and polymer; they could be explained by the same mechanism at all wavelengths.

In this paper we report on the results obtained in the photosensitized decomposition of thiophene by SO_2 at room temperature. The absorption band of thiophene starts at 2600 Å, so wavelengths longer than 2600 Å were used. Different SO_2 and thiophene pressures were used, and the effects of absorbed intensity, added N_2, and added NO were examined.

The system SO_2–thiophene was also irradiated with high-intensity radiation of wavelengths longer than 3600 Å, *i.e.*, within the triplet band of the SO_2 electronic spectrum. The results show that $^3SO_2$ does not participate in the reactions with thiophene molecules.

Experimental Section

Matheson Co. SO_2 (Anhydrous), NO (Technical), CO (C.P.), and N_2 (prepurified) were used. The SO_2, which contained about 0.5% CS_2 and 0.1% H_2S as the only impurities, was purified by gas-solid chromatography on a silica gel column (3 ft long by 0.25 in. in diameter) using a programmed temperature rise from 170 to 250° and a helium flow rate of 60 cc/min. For NO, the fraction volatile at $-186°$ was used after degassing at $-196°$. The CO was passed through a trap filled with glass wool and immersed in liquid N_2 to remove the CO_2. The N_2 was used without further purification and contained only 660 ppm of O_2. Thiophene (Sharpless Chemical Inc.) was purified by gas-liquid chromatography on a 20 ft long column packed with 10% tricresyl phosphate on Chromosorb G (N.A.W.) at 100° and a helium flow rate of 60 cc/min. CF_3I was obtained from Peninsular Chem Research Co. The major impurity was C_2F_6 which was removed by using the fraction of CF_3I volatile at $-130°$ but condensable at $-160°$.

A cylindrical quartz cell 10 cm long by 5 cm in diameter attached to a conventional grease-free, high vacuum line was used. The radiation was from a Hanovia medium-pressure mercury U-tube lamp, type 30620. The products were condensed at $-196°$ and the H_2 produced was measured in a McLeod pressure gauge. All the condensable products were analyzed in a 40 ft by 0.25 in. column packed with 10% dimethylsulfolane on Chromosorb G (N.A.W.) at 0° with a helium flow rate of 40 cc/min, in conjunction with a Gow-Mac Thermistor detector operated at 0°. For the runs with added NO, the reaction products were condensed at $-186°$ and the noncondensable gases removed before analysis with the same gas chromatographic system as the one used for the other runs. The identification of the products, except CH_2CO, was performed by comparison of their gas chromatographic retention times with those of authentic commercial samples.

The identification of the CH_2CO was performed by photolyzing acetone, at room temperature, with 3130-Å radiation and comparing the retention time of the CH_2CO produced with the retention time of the supposed CH_2CO in our system. Thus calibrations were not made and the reported quantum yields are relative, probably only correct to a factor of 2 in absolute value.

Since polymer formation was observed, air was admitted to the cell and heated with an oxygen torch to about 500° after each experiment to remove polymer. Quantum yields of the products

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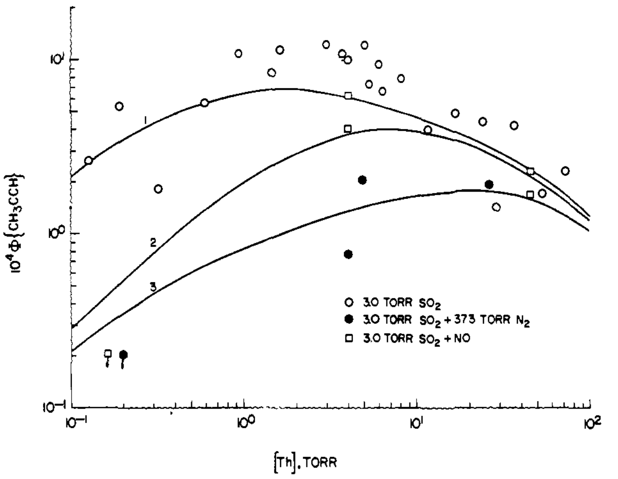

Figure 1. Plots of $\Phi\{CH_3CCH\}$ *vs.* thiophene pressure for experiments with 3.0 Torr of SO_2 at full lamp intensity. The solid lines are computed from the derived mechanism and the rate constant ratios listed in Table IV. Curve 1 corresponds to $\Phi\{CH_3CCH\}$ as computed from eq A ($[N_2] = 0$) and should fit the data points with no added gas. Curve 2 corresponds to $\Phi^*\{CH_3CCH\}$ as computed from eq C ($[N_2] = 0$) and should fit the data points with NO added. Curve 3 is the curve computed from eq A ($[N_2] = 373$ Torr) and corresponds to the data points with added N_2. The two data points with arrows indicate upper limits, as no CH_3CCH was detected.

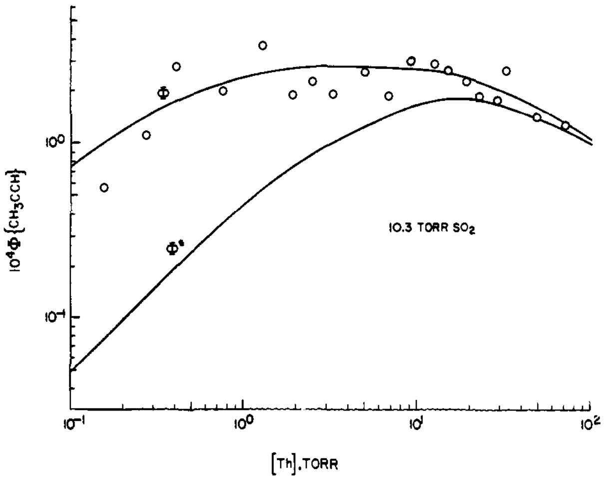

Figure 2. Plots of $\Phi\{CH_3CCH\}$ *vs.* thiophene pressure for experiments with 10.3 Torr of SO_2. The solid lines are computed from the derived mechanism and the rate constant ratios listed in Table IV. The upper curve corresponds to $\Phi\{CH_3CCH\}$ as computed from eq A and should fit the data points. The lower curve corresponds to $\Phi^*\{CH_3CCH\}$ as computed from eq C.

were measured utilizing CF_3I as actinometer. The C_2F_6 produced during the photolysis of CF_3I in the presence of mercury (to remove iodine) was measured in the McLeod gauge, trapping the nondecomposed CF_3I at −160°. The quantum yield for the production of C_2F_6 during the photolysis of CF_3I in the presence of mercury was taken as 0.5.[29]

Preliminary runs were performed using the radiation filtered through a Corning 0-54 filter which removes all the radiation below 3000 Å. The absolute yield of the products was very small. Then, in order to increase the absolute amount of products produced, the full Hg arc was used.

Equal optical densities of reagent and actinometer gases were used to avoid errors due to the uncertain path length of light. The ratio of the average extinction coefficient for the SO_2 to the average extinction coefficient for the CF_3I for the three principal wavelengths used (3130, 3022, and 2967 Å) was taken as 9.[30,31] Fortunately, the relative extinction coefficient at the three wavelengths is similar in both CF_3I and SO_2, so that actinometry errors are minimal.

Several runs were performed in a cylindrical Pyrex cell 100 cm long by 5 cm in diameter. The radiation in these runs was from a Hanovia 418C-9 Xe arc (800 W) filtered through a Plexiglass filter which removed all the radiation below 3600 Å. The products of the irradiation of SO_2-thiophene mixtures in this system were analyzed following the same procedure described above. The products of the irradiation of SO_2-CO and SO_2-CO-N_2 mixtures in this system were analyzed on a 20 ft long by 0.25 in. diameter Porapak Q column at 0° with a helium flow rate of 60 cc/min.

Results

When mixtures of SO_2 and thiophene were irradiated with the full mercury arc (radiation principally at 3130, 3022, 2976 Å) at 25 ± 3°, the products of the reaction were: H_2 as the predominant product; CH_2CO, SCO, C_2H_2, CH_2CCH_2, CH_3CCH, CS_2, and CH_2CHCCH as significant products; and traces of C_2H_4 and C_3H_6. Polymer was also formed, but CO and CH_4 were absent. No additional products were found in the presence of N_2 or NO. Dark runs did not give any reaction products.

Table I shows the effect of extent of conversion on the product quantum yields. The ± values reported for the reactant pressures do not reflect uncertainties in measurement, but rather variation in the experimental parameters. For short irradiation times, all the measurable product yields were independent of time to within the experimental uncertainty, which was large because of the small yields. The C_2H_4 and C_3H_6 yields were so small that they were ignored. It is difficult to see how they could be initial products of the reaction. To check that thiophene was not photolyzing by itself with the wavelengths used in this study, pure thiophene was irradiated under the same conditions used in a typical run and no products were found.

The product quantum yields for three different SO_2 pressures (3.0, 10.3, and 50.1 Torr) and different thiophene pressures are listed in Table II. From the results it can be seen that there are two different kinds of products. One group consists of C_2H_2, CH_2CCH_2, CH_3CCH, CS_2, and CH_2CHCCH. We call these products type I products because they are the same as those found in the short-wavelength photolysis of pure thiophene.[28] Except possibly for C_2H_2, they are produced in the same ratios as in the direct photolysis. They must come from the decomposition of excited thiophene molecules produced by an energy-transfer process between an excited SO_2 molecule and a ground-state thiophene molecule. The quantum yields of the type I products increase by increasing the thiophene pressure for low thiophene pressures, reach a maximum of about 2–10 Torr of thiophene, and then drop at higher thiophene pressures.

Increasing the SO_2 pressure reduces the quantum yields of these products. These results are shown graphically in Figures 1–3 for CH_3CCH. CH_3CCH was selected as the typical product since during the photochemical study of pure thiophene[28] it was found that CH_3CCH was the only product coming directly from an excited thiophene molecule in a unimolecular step, without requiring an additional intermediate.

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Table I. Effect of Irradiation Time on Product Yields[a]

Irradiation time, min	$10^4\Phi\{H_2\}$	$10^4\Phi$-$\{CH_2CO\}$[b]	$10^4\Phi\{SCO\}$	$10^4\Phi\{C_2H_2\}$	$10^4\Phi$-$\{CH_2CCH_2\}$	$10^4\Phi$-$\{CH_3CCH\}$	$10^4\Phi\{CS_2\}$	$10^4\Phi$-$\{CH_2CHCCH\}$
60.0	7.8	0.38	0.12	1.88	0.57	0.45		1.52
120.0		0.14	0.05	1.58	0.46	0.26	0.53	1.93
120.0	6.0	0.16	0.12	1.93	0.60	0.34		
180.0	7.8	0.19	0.14	1.81	0.53	0.37	0.60	1.75
300.0	6.2	0.25	0.22	1.97	0.47	0.33	0.52	1.71

[a] $[SO_2]$ = 25.0 ± 0.5 Torr, [Th] = 18.2 ± 0.3 Torr. I_a = 196 μ/min. [b] Relative yields. Calibration uncertain to a factor of 2.

Table II. Photolysis of SO_2 with a Medium-Pressure Mercury Arc at 25 ± 3° in the Presence of Thiophene

[Th], Torr	Irradiation time, min	I_a, μ/min	$10^4\Phi\{H_2\}$	$10^4\Phi$-$\{CH_2CO\}$[a]	$10^4\Phi$-$\{SCO\}$	$10^4\Phi$-$\{C_2H_2\}$	$10^4\Phi\{CH_2$-$CCH_2\}$	$10^4\Phi$-$\{CH_3CCH\}$	$10^4\Phi$-$\{CS_2\}$	$10^4\Phi\{CH_2$-$CHCCH\}$
				$[SO_2]$ = 3.0 ± 0.1 Torr						
0.128	243.0	7.10	246	4.0	7.04	42.6	6.95	2.57	8.94	19.8
0.192	243.0	7.10	141	2.18	3.60	43.0	11.1	5.25	10.7	
0.320	267.0	9.24	136	0.80	3.01	66.0	15.7	1.80	29.0	11.7
0.602	211.0	14.64	118	1.12	2.18	60.5	11.5	5.55	34.0	11.2
0.935	180.0	14.64	174	0.62	1.84	65.2	12.2	10.8	13.2	30.3
0.987	1287.0	0.69		4.4	4.9	83	20	12.6		58
1.435	241.0	9.24	109	0.54		68.0	21.8	8.3	11.7	34.8
1.615	90.0	14.64	92.5	0.57	1.22	69.1	13.2	11.4		95.5
2.42	90.0	14.64	69.5	1.14	0.92	66.5	15.4			
3.00	180.0	14.64	88.2	0.73	1.18	79.2	15.7	12.1	11.3	71.5
3.67	123.0	9.24	96	0.62	1.07	104	18.9	10.9		129
4.02	91.0	14.64	45.7		0.67		13.9	9.95	4.70	
4.08	1008.0	0.69		9.1	1.37	94	23.5	10.7	19.7	80.0
4.87	91.0	14.64	59.5		1.32	70.1	21.9	12.0	6.60	69.0
5.27	188.0	9.24	87	0.60	1.88	62.4	19.0	7.21	22.3	48.0
6.14	124.0	14.64	67.6	0.48	1.03	61.0	9.85	6.65	2.74	125
7.04	180.0	12.2	47		1.17	51.7	12.8	9.50	8.90	55.5
8.42	180.0	14.64	34.9	0.80	0.76	46.7	9.95	7.80	16.6	51.2
11.51	225.0	14.64	28.0	0.38	0.25	23.8	3.60	3.93	1.67	30.7
16.8	204.0	12.2	30.0			15.0	8.07	4.90	8.14	21.5
23.9	182.0	12.2	19.0	0.19	0.42	12.4	5.08	4.38		
28.3	190.0	9.24	27.9	0.43	0.69	21.0	5.15	1.40	12.8	13.3
36.8	222.0	9.24	24	0.36	0.52	20.4	3.85	4.13		36.6
49.2	697.0	0.69			0.21	5.7	3.8	2.2		12.4
52.9	247.0	9.24	14.5	0.60	0.47	11.9	2.48	1.71		14.3
71.2	256.0	9.24	10.3	0.37	0.45	12.2	3.09	2.26	2.73	17.4
				$[SO_2]$ = 10.3 ± 0.2 Torr						
0.153	120.0	39.9	50.9	0.53	0.56	3.82	0.98	0.55		
0.269	180.0	39.9	46.7	0.79	0.79	5.83	0.89	1.11		
0.410	224.0	39.9	68.2	1.09	1.46	8.52	1.43	2.68	2.88	2.61
0.756	180.0	39.9	50.9	0.63	0.83	9.07	1.84	1.97	4.65	1.93
1.294	180.0	39.9	46.7	0.61	0.79	11.00	2.70	3.53	3.10	2.94
1.923	240.0	39.9	44.6	0.55	0.86	12.15	2.79	1.85	3.99	7.45
2.50	210.0	39.9	36.4	0.36	0.51	12.70	2.70	2.22	2.64	6.40
3.29	240.0	39.9	31.8	0.56	0.65	11.85	3.34	1.90	2.68	9.28
5.00	140.0	39.9	43.6		0.92	14.05	4.05	2.57	2.93	
6.91	150.0	39.9	30.6	0.53	0.61	12.80	2.92	1.86	2.09	12.90
9.12	180.0	39.9	25.5	0.52	0.53	11.70	2.88	1.93	3.33	12.1
10.43	150.0	39.9	20.3	0.27	0.68	13.30	3.70		2.93	12.26
12.82	174.0	39.9	26.3	0.37	0.58	12.05	3.94	2.80		11.4
15.14	121.0	39.9	25.3	0.37	0.36	11.85	2.45	2.56	1.72	11.50
19.21	180.0	39.9	16.8	0.46	0.45	10.40	2.70	2.22	2.56	10.90
23.23	100.0	39.9	18.3	0.41	0.34	10.50	2.22	1.86	2.78	8.95
29.10	210.0	39.9	14.5	0.98	0.47	8.83	2.36	1.75	2.43	9.31
33.24	180.0	39.9	10.0	0.36	0.30	9.95	2.20	2.60		9.41
48.53	189.0	19.4	16.5	0.61	0.48	8.90	2.47	1.40	3.20	
70.38	189.0	19.4	16.5	1.43	0.55	7.25	1.64	1.25		10.20
				$[SO_2]$ = 50.1 ± 0.1 Torr						
0.660	617.0	70.88	9.0	0.46	0.13	0.41	0.04	0.05	0.31	0.49
0.974	300.0	85.28	8.3	0.35	0.07	0.51	0.11	0.21		0.29
2.21	180.0	85.28	20.0	0.71	0.41	2.43	1.25	0.81	1.12	3.66
4.10	360.0	70.88	10.7	0.55	0.24	1.35	0.31	0.26	0.50	1.36
5.52	324.0	85.28	16.5	0.63	0.39	2.96	0.85	1.46	0.49	1.40
9.31	517.0	70.88	10.0	0.63	0.28	1.75	0.39	0.32	0.50	2.17
15.66	304.0	85.28	8.2	0.45	0.29	1.81	0.57	0.72	0.53	1.51
68.30	253.0	85.28	4.2	0.31	0.24	1.23	0.31	0.48	0.68	0.73

[a] Relative yields. Calibration uncertain to a factor of 2.

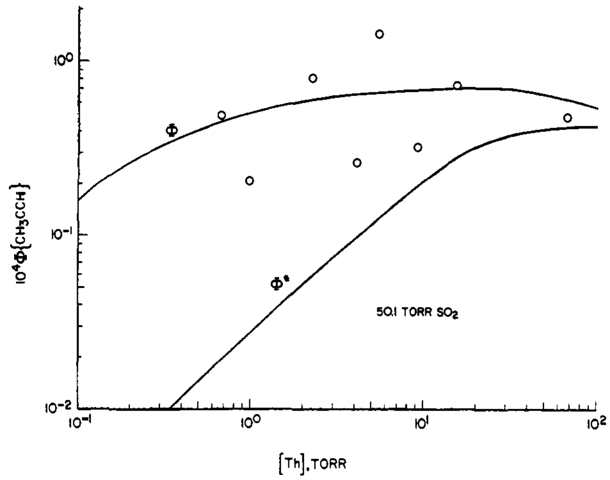

Figure 3. Plots of $\Phi\{CH_3CCH\}$ *vs.* thiophene pressure for experiments with 50.1 Torr of SO_2. The solid lines are computed from the derived mechanism and the rate constant ratios listed in Table IV. The upper curve corresponds to $\Phi\{CH_3CCH\}$ as computed from eq A and should fit the data points. The lower curve corresponds to $\Phi^*\{CH_3CCH\}$ as computed from eq C.

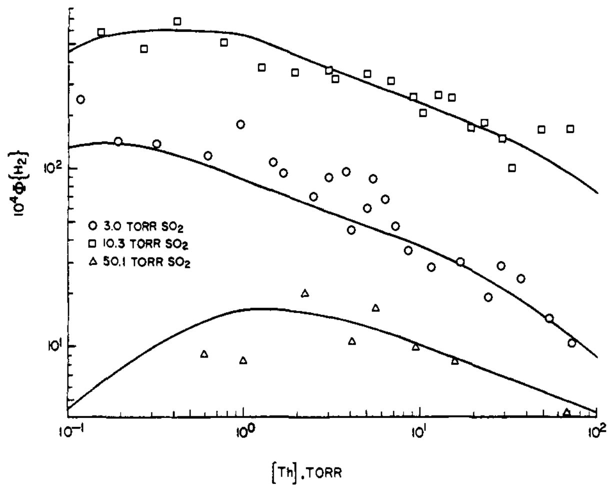

Figure 4. Plots of $\Phi\{H_2\}$ *vs.* thiophene pressure. The solid lines are computed from eq B ($[N_2] = 0$) and the rate constant ratios listed in Table IV. Both the data points and computed curve for 10.3 Torr of SO_2 have been shifted upward by a factor of 10 for clarity.

The second group of products, not produced in the direct irradiation of thiophene, is called type II products. This group consists of H_2, CH_2CO, and SCO as major constituents. Some of the acetylene produced also probably belongs to this group.

The quantum yields of the type II products decrease by increasing the thiophene pressure for the lowest SO_2 pressure. For the other two SO_2 pressures studied they increase somewhat by increasing the thiophene pressure for low thiophene pressures, reach a maximum, and then decrease at high thiophene pressure. The quantum yields of these products decrease as the SO_2 pressure is raised. This behavior is shown graphically in Figure 4 for H_2 and in Figures 5–7 for SCO.

The effect of absorbed intensity also is shown in Table II. For three runs at 3.0 Torr of SO_2 the absorbed intensity, I_a, was reduced to 0.69 μ/min, a reduction by a

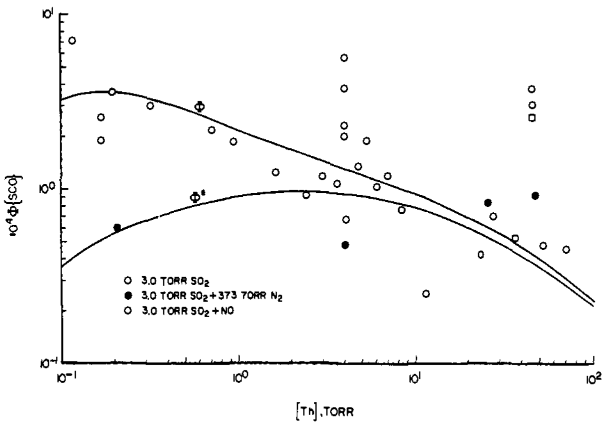

Figure 5. Plot of $\Phi\{SCO\}$ *vs.* thiophene pressure for experiments with 3.0 Torr of SO_2 at full lamp intensity. The solid lines are computed from the derived mechanism and the rate constant ratios listed in Table IV. The upper curve corresponds to $\Phi\{SCO\}$ as computed from eq B and β ($\Phi\{SCO\} = \beta\Phi\{H_2\}$) and should fit the data points with no added gas. The lower curve corresponds to $\Phi^*\{SCO\}$ as computed from eq F and β ($\Phi^*\{SCO\} = \beta\Phi^*\{H_2\}$) and should fit the data points with N_2 added.

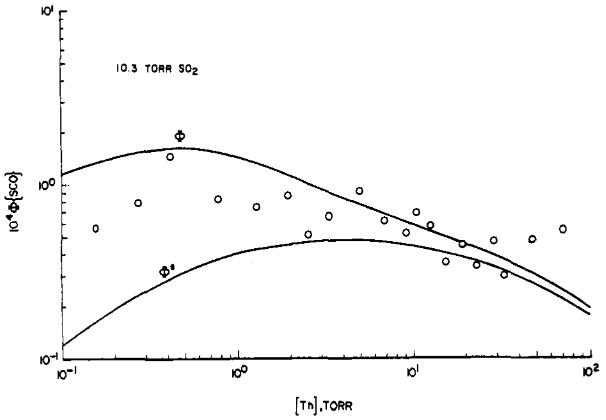

Figure 6. Plot of $\Phi\{SCO\}$ *vs.* thiophene pressure for experiments with 10.3 Torr of SO_2. The solid lines are computed from the derived mechanism and the rate constants listed in Table IV. The upper curve corresponds to $\Phi\{SCO\}$ as computed from eq B and β ($\Phi\{SCO\} = B\Phi\{H_2\}$) and should fit the data points. The lower curve corresponds to $\Phi^*\{SCO\}$ as computed from eq F and β ($\Phi^*\{SCO\} = \beta\Phi^*\{H_2\}$).

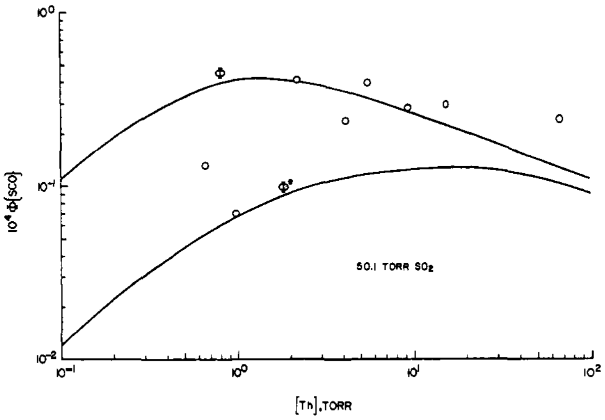

Figure 7. Plot of $\Phi\{SCO\}$ *vs.* thiophene pressure for experiments with 50.1 Torr of SO_2. The solid lines are computed from the derived mechanism and the rate constant ratios listed in Table IV. The upper curve corresponds to $\Phi\{SCO\}$ as computed from eq B and β ($\Phi\{SCO\} = \beta\Phi\{H_2\}$) and should fit the data points. The lower curve corresponds to $\Phi^*\{SCO\}$ as computed from eq F and β ($\Phi^*\{SCO\} = \beta\Phi^*\{H_2\}$).

Table III. Effect of Added Gases on Product Yields[a]

[Th], Torr	[X], Torr	Irradiation time, min	$10^4\Phi$-$\{CH_2CO\}$[b]	$10^4\Phi$-$\{SCO\}$	$10^4\Phi\{C_2H_2\}$	$10^4\Phi$-$\{CH_2CCH_2\}$	$10^4\Phi$-$\{CH_3CCH\}$	$10^4\Phi\{CS_2\}$	$10^4\Phi$-$\{CH_2CHCCH\}$
X = NO									
0.166	0.150	952.0	2.75	1.90		<0.2	<0.2	<0.4	<0.8
0.166	0.900	1201.0	2.68	2.56	0.46	<0.2	<0.2	<0.3	<0.6
0.166	10.96	1237.0	2.71	0.93	0.34	0.84	<0.2	<0.3	<0.6
0.166	75.8	688.0	3.40	0.71	1.96	0.21	<0.2	<0.5	<1.0
4.05	0.100	247.0	0.73	3.75	40.0	10.4	7.0	17.0	35.2
4.05	0.430	224.0	0.45	1.97	17.7	9.95	8.75	12.2	31.0
4.05	1.64	261.0	2.23	5.72	22.8	13.0	7.8	10.8	30.3
4.05	12.34	320.0	0.87	2.27	18.2	6.30	5.4	5.03	28.6
4.05	191.4	303.0	5.30	7.18	19.8	4.00	3.08	5.47	11.0
46	10	268.0		2.50	13.3	2.98	1.64	6.25	13.2
46	82	223.0	7.10	3.68	16.5	3.77	2.28	2.74	3.93
46	144	207.0	8.60	3.00	12.6	2.46	1.12		11.8
X = N_2									
0.205	373	693.0	1.19	0.60	0.50	<0.2	<0.2	<0.5	<1.0
4.01	370	189.0	2.90	0.48	10.1	1.60	0.75	1.63	5.7
26.45	376	620.0	3.60	0.84	13.2	1.92	1.74	1.62	6.45
47.38	375	249.0	2.91	0.91	16.0	2.64	2.04	1.83	9.8

[a] $[SO_2] = 3.0 \pm 0.1$ Torr, $I_a = 13.5 \pm 1.4\ \mu$/min. [b] Relative yields. Calibration uncertain to a factor of 2.

factor of 13.4–21. The quantum yields of product formation were not affected except for CS_2 and CH_2CO. The quantum yield of CS_2 formation, $\Phi\{CS_2\}$, increases markedly as I_a was reduced in the one run for which data were available. This effect is the same as in the direct photolysis of thiophene.[28] For CH_2CO, the quantum yield is also markedly enhanced at the lower intensity.

Besides the intensity effect on $\Phi\{CS_2\}$ and $\Phi\{CH_2CO\}$, the values obtained show extremely large scatter, which reflects the experimental difficulty for analysis of these products. The same large scatter for $\Phi\{CS_2\}$ was observed in the direct irradiation of thiophene.[28]

Table III shows the effect of added N_2 and NO to the system. The NO addition was done at 3 Torr of SO_2 and at three different thiophene pressures.

The addition of NO at low thiophene pressures does not change the values for the quantum yields of the type II products within the experimental error but drastically reduces those for the type I products.

The addition of NO when the thiophene pressure is 4 Torr (*i.e.*, the region at which the type I products reach a maximum) reduces the amount of type I products by about 30% (the data are shown in Figure 1 for CH_3CCH) but increases the type II products.

The NO addition does not affect the type I products at high thiophene pressure but markedly enhances the type II products.

The effect of the addition of N_2 on the CH_3CCH production is shown in Figure 1. The addition of N_2 lowers $\Phi\{CH_3CCH\}$, the effect being more pronounced as the thiophene pressure is reduced. The effect on the other physical products is qualitatively the same. The N_2 effect on $\Phi\{SCO\}$ is shown graphically in Figure 5. In this case, the addition of N_2 drastically reduces the SCO production at low thiophene pressure but does not affect it at thiophene pressures larger than 4 Torr.

Several mixtures were irradiated with wavelengths longer than 3600 Å in the long vessel (100 cm) with a very intense source (800-W Xe lamp) of radiation. A 24-hr irradiation of a mixture of 4 Torr of thiophene and 3 Torr of SO_2, where maximum product formation occurred with a full Hg arc, did not give any products. In order to check if the SO_2 was actually excited to the triplet state in these experiments, mixtures of SO_2 and CO were irradiated under similar conditions and CO_2 was actually found as the reaction product. Addition of N_2 to the SO_2–CO mixtures reduced CO_2 production confirming that $^3SO_2$ directly produced by the absorption of radiation at these wavelengths is responsible for production of CO_2.

By comparison of the SO_2–thiophene and SO_2–CO systems, the quantum yields of product formation in the SO_2–thiophene system must be $<10^{-3}$ of the CO_2 yield in the SO_2–CO system. In the SO_2–CO system, $\Phi\{CO_2\} < 10^{-1}$.[24] Also for radiation between 2650 and 3130 Å, the formation of $^3SO_2$ occurs less than 10% of the time.[7,32,33] Therefore with radiation at 3130 Å, the quantum yield of product formation in the SO_2–thiophene system from $^3SO_2$ is $<10^{-5}$, which is negligible.

Discussion

To account for the results found in the SO_2–CO and SO_2–C_2F_4 systems, the intervention of two new nonemitting states of SO_2 was postulated.[27] Those states were a singlet called SO_2* and a triplet called SO_2**. The mechanism outlined in the introduction was slightly modified to account for these states. Also at the pressures used in this study (>3.0 Torr of SO_2) the first-order steps, reactions 2 and 3, are known to be unimportant.[3,4] The mechanism for pure SO_2 becomes

$$SO_2 + h\nu \longrightarrow {}^1SO_2 \qquad (I_a)$$

$$^1SO_2 + SO_2 \longrightarrow {}^3SO_2 + SO_2 \qquad (1b)$$

$$\longrightarrow SO_2^* + SO_2 \qquad (1c)$$

$$SO_2^* \longrightarrow SO_2^{**} \qquad (5)$$

$$SO_2^* + SO_2 \longrightarrow SO_2^{**} + SO_2 \qquad (6)$$

$$SO_2^{**} \longrightarrow SO_2 \qquad (7)$$

The fate of $^3SO_2$ has been omitted, since our results in which $^3SO_2$ was produced directly show that $^3SO_2$ does not interact with thiophene. (It should be mentioned

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(32) T. N. Rao and J. G. Calvert, *J. Phys. Chem.*, 74, 681 (1970).

(33) A. Horowitz and J. G. Calvert, private communication, 1971.

that $^3SO_2$ produced directly by 3660-Å radiation may have more vibrational energy, and thus be more reactive, than $^3SO_2$ produced by intersystem crossing from $^1SO_2$, a collisionally induced process producing vibrationally thermally equilibrated $^3SO_2$.)

Since the production of type I products is not completely quenched by adding excess N_2, the states principally responsible for type I product formation should be those not quenched by N_2, *i.e.*, the nonemitting states. At low thiophene pressures, the addition of small amounts of NO ($\sim$ 1 Torr) drastically inhibits product formation, whereas at high thiophene pressure, NO has no effect Cehelnik, *et al.*,[27] have shown that about 1 Torr of NO removes about 75% of SO_2^{**}. Consequently SO_2^{**} must be the important sensitizer at low thiophene pressures, and SO_2^*, the important sensitizer at high thiophene pressures.

In the case of type II products, the addition of NO either has no effect or increases CH_2CO and SCO formation (no data are available with H_2 since NO interfered with the analytical scheme). While the possibility of SO_2^{**} playing some role cannot be excluded, it cannot be the important precursor to type II product formation, since it is readily scavenged by NO. For simplicity we will assume that the type II products arise solely from $^1SO_2$ and SO_2^*.

The additionally required steps are

$$^1SO_2 + Th \longrightarrow SO_2 + Th^{II} \quad (8a)$$

$$\longrightarrow SO_2^* + Th \quad (8b)$$

$$SO_2^* + Th \longrightarrow SO_2 + Th^{I} \quad (9a)$$

$$\longrightarrow SO_2 + Th^{II} \quad (9b)$$

$$SO_2^{**} + Th \longrightarrow SO_2 + Th^{I} \quad (10a)$$

$$\longrightarrow SO_2 + Th \quad (10b)$$

where Th is ground-state thiophene, and the superscripts I and II represent the excited states which lead to type I and type II products, respectively.

The fate of Th^I is well known from the work of Wiebe and Heicklen.[28]

$$Th^{I} \longrightarrow \text{type I products} \quad (11)$$

$$Th^{I} + Th \longrightarrow 2Th \quad (12)$$

$$Th^{I} + SO_2 \longrightarrow Th + SO_2 \quad (13)$$

The quenching of Th^I by SO_2, reaction 13, was not studied by Wiebe and Heicklen, but C_2H_4, CO_2, and O_2 all reduced product formation. Presumably SO_2 behaves similarly.

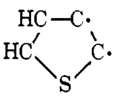
The simplest reaction scheme for type II product formation is

$$Th^{II} \longrightarrow H_2 + C_4H_2S \quad (14)$$

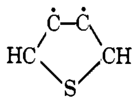
$$Th^{II} + Th \longrightarrow 2Th \quad (15)$$

$$Th^{II} + SO_2 \longrightarrow Th + SO_2 \quad (16)$$

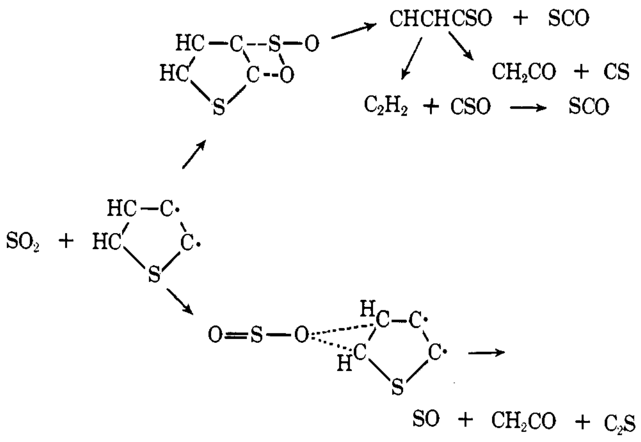
The C_4H_2S intermediate may be either



or



The former could eject C_2H_2 or react with SO_2 to give the other type II products



The CS, C_2S, and SO would be incorporated into the polymer. The reason for the enhancement in $\Phi\{CH_2CO\}$ when excess N_2 was added is not clear, but it cannot be due to stabilization of "hot" CH_2CO, since then CO should have been produced at low pressures contrary to our observations.

The above mechanism does not include a direct transfer of an oxygen atom from electronically excited SO_2 to thiophene. Oxygen atom transfer was the exclusive photochemical process in the CO and C_2F_4 systems, and perhaps CH_2CO is produced in this way in the present study. However CH_2CO is a minor product; thus oxygen atom transfer, if it does occur, is not a major photochemical process in the SO_2–thiophene system.

Finally to complete the mechanism the quenching steps of N_2 are included

$$^1SO_2 + N_2 \longrightarrow SO_2^* + N_2 \quad (17)$$

$$Th^{I} + N_2 \longrightarrow Th + N_2 \quad (18)$$

$$Th^{II} + N_2 \longrightarrow Th + N_2 \quad (19)$$

The quenching of $^1SO_2$ by N_2 must produce SO_2^* at least part of the time as shown by Cehelnik, *et al.*[27] Similarly the same must be true here, since products were produced in the presence of excess N_2. Neither SO_2^* nor SO_2^{**} is quenched by N_2 as deduced previously.[27]

The mechanism predicts that

$$\Phi\{CH_3CCH\} = \Phi^*\{CH_3CCH\} + \Phi^{**}\{CH_3CCH\} \quad (A)$$

$$\Phi\{H_2\} = \Phi^1\{H_2\} + \Phi^*\{H_2\} \quad (B)$$

where Φ^*, Φ^{**}, and Φ^1 are those portions of Φ arising from SO_2^*, SO_2^{**}, and $^1SO_2$, respectively. Specifically these are

$$\Phi^*\{CH_3CCH\} = \alpha k_{9a}k_{11}[Th]/(k_5 + k_6[SO_2] + k_9[Th])(k_{11} + k_{12}[Th] + k_{13}[SO_2] + k_{18}[N_2]) \quad (C)$$

$$\Phi^{**}\{CH_3CCH\} = \alpha k_{10a}k_{11}[Th](k_5 + k_6[SO_2])/(k_5 + k_6[SO_2] + k_9[Th])(k_7 + k_{10}[Th])(k_{11} + k_{12}[Th] + k_{13}[SO_2] + k_{18}[N_2]) \quad (D)$$

$$\Phi^1\{H_2\} = k_{8a}k_{14}[Th]/(k_1[SO_2] + k_8[Th] + k_{17}[N_2])(k_{14} + k_{15}[Th] + k_{16}[SO_2] + k_{19}[N_2]) \quad (E)$$

$$\Phi^*\{H_2\} = k_{9b}k_{14}[Th]/(k_5 + k_6[SO_2] + k_9[Th])(k_{14} + k_{15}[Th] + k_{16}[SO_2] + k_{19}[N_2]) \quad (F)$$

where α is that fraction of reaction 11 which leads to CH_3CCH formation, $k_1 \equiv k_{1b} + k_{1c}$, $k_8 \equiv k_{8a} + k_{8b}$, $k_9 \equiv k_{9a} + k_{9b}$, and $k_{10} \equiv k_{10a} + k_{10b}$. In deriving eq C–F it was further assumed, for simplicity, that $k_{1c} \simeq k_1$ and $k_{8b} \simeq k_8$. It has been shown[7] that $k_{1b} = 0.08k_1$, so that the former assumption is justified and consistent with the interpretation of Cehelnik, *et al.*[27] We shall soon show that the results can be fitted with $k_{8a}/k_8 = 1.1 \times 10^{-3}$, so that the latter assumption is also justified.

By a process of curve fitting a number of rate constant ratios were obtained and they are listed in Table IV. With these rate constant ratios we have computed $\Phi\{CH_3CCH\}$ in the absence and presence of N_2, and $\Phi^*\{CH_3CCH\}$ and $\Phi\{H_2\}$ in the absence of N_2.

Table IV. Rate Constant Ratios

Ratio	Value	Units
α	0.077	None
k_5/k_{9a}	38.2	Torr
k_6/k_{9a}	9.6	None
k_{9b}/k_{9a}	2.0	None
k_{12}/k_{11}	1.7	$Torr^{-1}$
k_{13}/k_{11}	0.97	$Torr^{-1}$
k_{18}/k_{11}	0.010	$Torr^{-1}$
k_7/k_{10a}	100	Torr
k_{10}/k_{10a}	300	None
k_1/k_{8a}	24	None
k_8/k_{8a}	900	None
k_{15}/k_{14}	6.6	$Torr^{-1}$
k_{16}/k_{14}	0.145	$Torr^{-1}$
β	0.0256	None

The computed curves for $\Phi\{CH_3CCH\}$ in the absence of added gases are shown in Figures 1–3 for the three SO_2 pressures used. In Figure 1, this curve is curve 1. It fits the data well at low and high pressures of thiophene but is about 30% low at intermediate pressures. This fit is not too bad, considering the scatter in the data and the simplifying assumptions in the mechanism. The data are well fitted at 10.3 Torr of SO_2 (Figure 2) and 50.1 Torr of SO_2 (Figure 3).

With N_2 present, $\Phi\{CH_3CCH\}$ was computed only for 3.0 Torr of SO_2, since experiments were done only at this SO_2 pressure. The computed results are given by curve 3 in Figure 1, and it adequately fits the badly scattered data.

The curves computed for $\Phi^*\{CH_3CCH\}$ should correspond to runs with added NO (since >3 Torr NO was shown[27] to scavenge SO_2^{**}). This will only be true if NO is not an efficient scavenger of Th^I. To test this hypothesis, 1.25 Torr of Th was irradiated with radiation from a Phillips 25-W cadmium resonance lamp (mainly 2288 Å, but also some 2265- and 2144-Å radiation) at room temperature in the absence and presence of 1.3 Torr of NO. The results are shown in Table V and are identical with the results with added O_2.[28] The C_2H_2, CH_2CCH_2, and CH_3CCH yields are unaffected, $\Phi\{CH_2CHCCH\}$ drops by about $^1/_2$ its value, and $\Phi\{CS_2\}$ is substantially reduced when NO is added. For our purposes, the fact that $\Phi\{CH_3CCH\}$ is essentially unaffected substantiates the hypothesis. The curve for $\Phi^*\{CH_3CCH\}$ in Figure 1, *i.e.*, curve 2, fits the results with NO present at high thiophene pressures, is consistent with the data point at low thiophene pressure (even though the data point represents an upper limit, it must be essentially correct from an examination of $\Phi\{CH_2CCH_2\}$ in the same run), and is satisfactory at intermediate pressures. With 4 Torr of thiophene, curve 2 should actually have passed between the two data points with NO added, since the upper point was for a run with insufficient NO to completely scavenge SO_2^{**}, but the lower point was for a run with 191 Torr of NO, so that some quenching of Th^I should have occurred.

Table V. Photolysis of Thiophene with a Cadmium Resonance Lamp[a]

[NO], Torr	Φ-$\{C_2H_2\}$	$\Phi\{CH_2$-$CCH_2\}$	Φ-$\{CH_3CCH\}$	$\Phi\{CS_2\}$	$\Phi\{CH_2$-$CHCCH\}$
0	0.057	0.020	0.0071	0.029	0.072
1.3	0.045	0.016	0.0061	0.010	0.030

[a] [Th] = 1.25 Torr, irradiation time = 30 min, I_a = 37 μ/min.

The computed curves for $\Phi\{H_2\}$ are shown in Figure 4, and they adequately represent the data. If $\Phi\{SCO\}$ is always some constant fraction, β, of $\Phi\{H_2\}$, then $\Phi\{SCO\}$ and $\Phi^*\{SCO\}$ can be computed also. This has been done, using $\beta = 0.0256$, and these curves are shown in Figures 5–7. The curves for $\Phi\{SCO\}$ fit the data reasonably well, except for low pressures of thiophene at 10.3 and 50.1 Torr of SO_2. Since β may not be a constant, the mechanism may be oversimplified. Also the data are quite scattered. Therefore the degree of fit that is achieved is acceptable. At least the appropriate trends are reproduced.

The computed curve for $\Phi^*\{SCO\}$ in Figure 5 should correspond to the data points with excess N_2 added. Again the fit is hardly ideal, but it is also not too bad.

Finally it is necessary to see if the rate constant ratios in Table IV agree with the previous studies. Cehelnik, *et al.*,[27] found k_5/k_6 = 4.6 Torr in the SO_2–CO system and 3.5 Torr in the SO_2–C_2F_4 system. Our results lead to a value of 4.0 Torr in excellent agreement with the earlier findings.

The relative quenching of Th^I by Th, SO_2, and N_2 is 1.7/0.97/0.10, a trend expected considering the complexity of the quenching gases. Wiebe and Heicklen[28] did not use SO_2 or N_2 as quenching gases in their studies, but they found that Th was 5–9 times as efficient as O_2 (which should be similar to N_2). Furthermore Wiebe and Heicklen found α to be between 0.041 and 0.074, whereas we obtain 0.077. Finally the ratio k_{12}/k_{11} was found to vary with the energy input into Th^I as shown in Table VI. The values are listed in order of decreasing energy input into the molecule, and k_{12}/k_{11} increases, as expected. Our value fits nicely the trend found in the earlier work.

Table VI. Values of k_{12}/k_{11} for Various Conditions

k_{12}/k_{11}, $Torr^{-1}$	Conditions
0.021	2139 Å, 305°[a]
0.18	2288 Å, 305°[a]
0.28	2139 Å, 25°[a]
1.13	2288 Å, 25°[a]
1.7	This work

[a] From Wiebe and Heicklen.[28]

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