Ultraviolet Absorption Spectra and the Chemical Mechanism of CS2–O2 Explosions

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Citation: The Journal of Chemical Physics **26**, 1309 (1957); doi: 10.1063/1.1743513
View online: http://dx.doi.org/10.1063/1.1743513
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/26/5?ver=pdfcov
Published by the AIP Publishing

ion should increase as the electron impact voltage is increased. In the present study the ratio of the abundance of the mass 6.5 peak to that of the mass 26 peak was examined as a function of the electron impact potential as it was varied from 12 to 75 volts. Within experimental error this ratio was found to be constant, independent of the electron accelerating voltage. We conclude, therefore, that the mechanism of the collision-induced dissociation process can involve an interaction between a residual gas molecule and an unexcited ion. This does not exclude the possibility of collision-induced dissociations occurring between excited ions and residual gas molecules.

ACKNOWLEDGMENTS

The authors gratefully acknowledge helpful discussions with J. F. Burns, A. E. Cameron, J. R. McNally, Jr., and H. W. Morgan of this laboratory and Professor H. E. Carr of the Alabama Polytechnic Institute. Our special thanks go to H. M. Rosenstock.†

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THE JOURNAL OF CHEMICAL PHYSICS VOLUME 26, NUMBER 5 MAY, 1957

Ultraviolet Absorption Spectra and the Chemical Mechanism of CS_2-O_2 Explosions*

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(Received November 21, 1955)

Ultraviolet absorption spectra have been obtained at various times during and after homogeneous explosions of carbon disulfide-oxygen mixtures thermally initiated at temperatures of 190 to 300°C. This has been accomplished by triggering a flash source of continuum by means of the early chemiluminescence of the explosion. These photographically recorded spectra show the presence, and the absorption intensity as a function of time, of CS, SO, SO_2, S_2O_2, S_2, CS_2 and a species which absorbs in a continuum, to which has been assigned the structure of a sulfur superoxide, SOO. Numerous conclusions have been reached from these data concerning the elementary chemical reactions that are involved in these experiments. A direct bimolecular reaction is postulated for the initiation process which produces the superoxide, and eventually free radicals. In the very early stages of the explosion, propagation proceeds via a slowly branching primary chain which involves an attack on the reactants by sulfur and oxygen atoms. As the branching reaction proceeds and the temperature increases, the mechanism undergoes a number of changes including an increase in the importance of a nonfree radical, bimolecular process. The explosion is especially interesting in that one of the final products, sulfur dioxide, does not appear in more than minor concentrations, almost characteristic of an intermediate, until the explosion is over. This is explained in terms of the reactions postulated.

I. INTRODUCTION

In a recent paper[1] by two of these authors, the technique and apparatus were described whereby flash absorption spectra in the ultraviolet were recorded for thermally initiated CS_2-O_2 explosions. The information thus obtained and its implications with respect to the chemical mechanism involved are now presented along with a few similar observations made with $COS-O_2$ mixtures.

Prior to the present work, the only extensive spectroscopic studies of CS_2 combustion involved the emission spectra of CS_2 flames in air and oxygen.[2-4] Very little had been done with absorption spectra of the flames[5] and no spectral studies of explosions had been made. The principal findings of these studies were the detection, usually through their emission spectra, of CS, S_2, and possibly SO, as intermediates. These species were detected always under the steady-state conditions of flames. In the present work, the absorption spectra of seven species, emitting and nonemitting, were followed as a function of time through all stages of the thermally initiated explosion. The molecules and radicals studied were CS, SO, S_2, S_2O_2, CS_2, SO_2 and a continuous absorber to which the superoxide structure SOO has been assigned.

As described in the previous publication, the chemiluminescence of the reaction was used to trigger the photoflash at any desired time in the period starting several milliseconds prior to the sharp rise in radiation emission and ending with the radiation peak. By means of a photomultiplier and thyratron delay circuit not previously discussed, this range has now been extended to record interesting phenomena occurring as early as

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* This research was performed under Contract AF 33(038)-20863 with the Chemistry Research Branch of Wright Air Development Center, Dayton, Ohio.

† Present address: Missile and Ordnance Systems Department, General Electric Company, Philadelphia 4, Pennsylvania.

[1] P. L. Hanst and A. L. Myerson, Rev. Sci. Instr. 25, 5, 469 (1954).

[2] A. Fowler and W. M. Vaidya, Proc. Roy. Soc. (London) A132, 310–330 (1931).

[3] H. J. Emeleus, J. Chem. Soc. 1926, 2948–2951.

[4] V. Kondratyev, Zhur. Fiz. Khim. 13, 1260–70 (1939).

[5] V. Kondratyev, Bull. acad. sci. U.R.S.S. Classe sci. chim. 501–558 (1940).

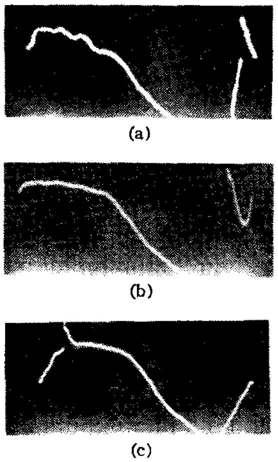

FIG. 1. Oscilloscope traces of light emission from CS_2-O_2 explosions. (Figure 1(a) has been retouched.) These traces were obtained with a recurrent, left-to-right sweep of 16.7 milliseconds duration. The initial rise begins in the second half of the sweep in all cases. The break in the rise of the explosion radiation is due to the photoflash emission. This is most clearly in evidence in trace (c).

100 msec before, and as late as 100 or so msec after, the peak of light emission from the explosion.

The results are described first in terms of the individual species, and then with respect to the interactions of these species during the induction period, the period of rapid chain-branching propagation and the post-explosion period.

II. EXPERIMENTAL

The apparatus and procedure have been described fully in the previous publication.[1] However, a number of important changes have been made since that time in widening the scope of the investigation and in the interest of reproducibility and efficiency.

It was found feasible and safe to mix the CS_2 and O_2 before allowing them to enter the thermostated absorption-explosion cell. This resulted in excellent reproducibility, in contrast to that previously encountered, using the technique of successive mixing. The premixing was also important from the viewpoint of explosion homogeneity, evidence for which is provided by the consistency, over all of the numerous explosions observed, of spectroscopic records of various species as a function of time. The only indication of inhomogeneity was the irregularity sometimes noted in oscilloscope traces of the explosion radiation as illustrated in (a) of Fig. 1. However, this irregularity can be readily and invariably eliminated by exploding mixtures only at temperatures and pressures corresponding to near-boundary conditions where long induction times (several seconds and longer) result. In every case, this produces smooth traces such as (b) and (c) of Fig. 1, probably because the long induction period permits interdiffusion and a homogeneous (slow) growth along the tube, up to the instant of explosion, of the metastable intermediates and chain carriers characteristic of a degenerate branched-chain process. The time at which the flash tube was fired during the explosions, is marked by the very sharp break or increase in light intensity superimposed on the emission trace.

It can be shown further that detonation waves cannot occur in these experiments and hence cannot account for the irregularities or oscillations when they do appear on the emission traces. Data obtained by P. Lafitte[6] show that in a tube 34 mm in diameter, which contains a mixture of $CS_2+3\ O_2$, a flame (spark initiated) must travel 85 cm before a detonation wave forms. Our observations were made at higher temperatures and apparently lower pressures than those of Lafitte's. Since both of these conditions retard the onset of detonation, the latter should be impossible in our tubes, which were 55 cm and 20 cm in length and 35 mm in diameter.

Also, the radiation traces and spectra cannot be interpreted in terms of the viewing of the normal propagation of a flame past the area of phototube observation, because of the time involved. The rate of normal flame propagation would be 200 cm/sec at most, which would result in a tube traversal of at least 140 msec (assuming that the flame begins in the middle of the tube) and a period of viewing the radiation equal to a major fraction of that time. This may be compared to the observed 10 or 15 msec duration of the light emission, including decay, from the explosion.

Improvements have also been made in the timing of the photoflash. The electronic circuit previously reported was changed to one applicable to a photomultiplier, which actuated a thyratron relay. A constant neutral light filter was used in front of the photomultiplier, and the time between the firing of the

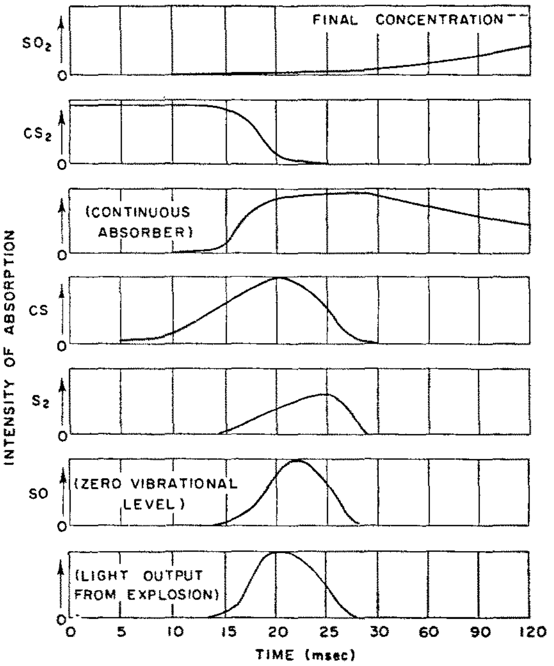

FIG. 2. Occurrence of free radicals and molecules during the CS_2-O_2 explosion. These curves represent estimated absorption intensities as a function of time, as determined from several hundred experiments.

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[6] P. Lafitte, Compt. rend. **177**, 178 (1923); **179**, 1394 (1924). Ann. Physik **10**, 4, 623 (1925).

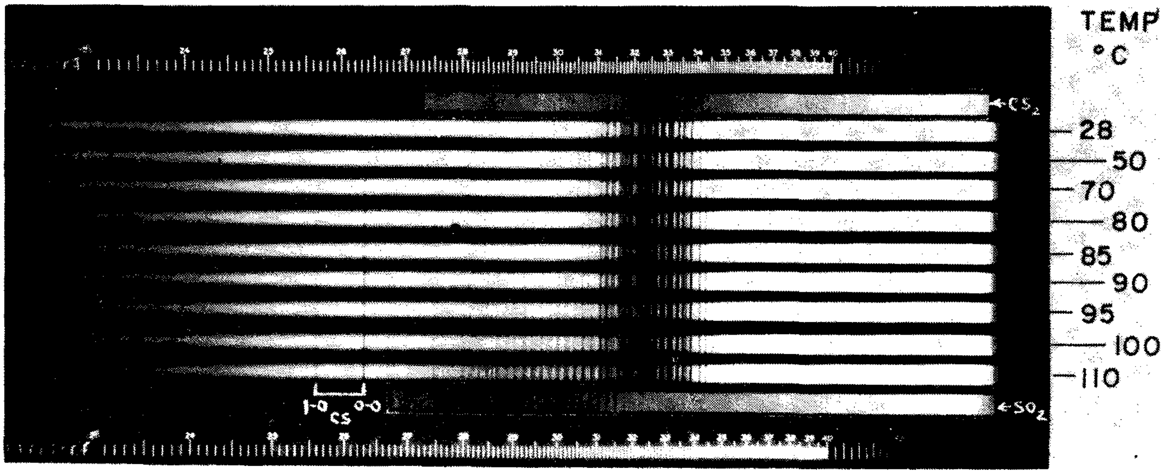

FIG. 3. Growth of CS and SO_2 in a nonexploding mixture of 25 mm of Hg of CS_2 and 75 mm of Hg of O_2 at temperatures of 28° to 110°C. The CS quickly attains a constant (steady-state) concentration which is an increasing function of temperature, while the SO_2 concentration increases with time.

thyratron and the triggering of the photoflash was determined and controlled by an electronic delay circuit which also employed a thyratron. By this method, it was possible to obtain spectra well in advance of the peak and well after the peak, as previously mentioned, and with excellent reproducibility and electronic stability. The medium quartz Hilger spectrograph previously employed was replaced by the large Bausch & Lomb Littrow of much greater dispersion.

A much larger flash tube of 4 mm inside diameter was used to discharge a 25-μf condenser at 4000 v, replacing a 6-μf condenser previously discharged at 4000 v. This tube provided a satisfactory continuum from 2000 A to 9000 A.

The carbon disulfide used was either provided in a pure state (99.99%) by Westvaco Chemical Corporation or purchased as a cp material and fractionated. Mass spectrometrically analyzed oxygen (99.9%) was obtained from Air Reduction Corporation. Carbonyl sulfide, COS, was prepared by the action of 40% H_2SO_4 on KCNS and then purified. Anhydrous SO_2 (99.7%) was obtained from the Mathieson Company.

III. IDENTIFICATION OF THE SPECTRA, AND THEIR OCCURRENCE AS A FUNCTION OF TIME

A summary of one aspect of the investigation is shown in semiquantitative form in Fig. 2. An estimate of the absorption intensity of each species as a function of time has been made from numerous plates, including reference spectra. The absorption intensity-time relationships are shown with reference to a typical oscilloscope trace of total radiation sketched at the bottom of the figures. Practically all the explosions resulted from mixtures under conditions corresponding to the first ignition limit. The partial pressure of CS_2 was, in the majority of experiments, equal to approximately 8 mm of Hg regardless of the ratio CS_2:O_2. The furnace temperatures were in the range 190–300°C.

Carbon Disulfide, CS_2

The decrease in concentration of CS_2 was readily followed by its complex system of headless bands in the wavelength region 3346–2993 A. In general, it can be concluded from inspection of many plates that a large fraction of the CS_2 has been consumed when the intensity of the radiation has reached its peak and that it has disappeared completely two to four milliseconds later. However, this does not indicate the absence of further reaction as evidenced by the further growth of the continuous absorber during the remaining 6 msec of radiation emission. The behavior and identity of this absorber will be discussed in detail in a later section.

Carbon Monosulfide, CS

CS has been identified in both heated (up to 100°C) nonexploding mixtures of CS_2-O_2, and in exploding mixtures. In the former case in which the CS spectrum is uncomplicated by other species, it has been identified by the band heads at 2575.6 A (0, 0—very strong), 2507.3 A (1, 0—strong), and 2444.8 A (2, 0—weaker). In Fig. 3 is shown a series of absorption spectra of 1:3 mixtures of CS_2:O_2 at temperatures varying from 28° to 110°C. The CS appears at surprisingly low temperatures in such mixtures, at least as low as 50°C. Its steady-state concentration is reproducibly dependent on the temperature. No trace of CS can be detected in absorption spectra of pure CS_2 at the same temperature.

The CS was followed during explosions mainly through its strong (0, 0) band (at 2575.6 A). It is the most prominent absorber in the exploding mixtures and increases in absorption intensity during the early stages of the reaction and apparently decreases with decreasing intensity of the explosion radiation. Its concentration is somewhat higher in 1:6 mixtures than in 1:3 mixtures of CS_2:O_2.

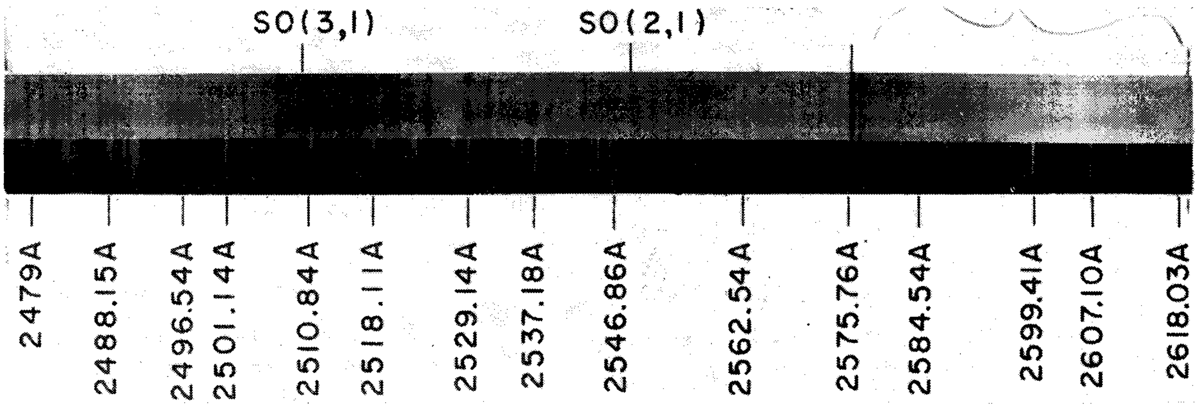

FIG. 4. (a) Absorption spectrogram of CS_2-O_2 explosion, 2479–2618 A. This spectrogram and the others of series 4, show the absorption bands of SO and S_2 in the spectral range 2479–3068 A. (Reference in this and all succeeding spectrograms is an iron arc.)

The Sulfur Molecule, S_2

Absorption bands of the S_2 molecule have been identified in the spectra of the exploding gases, in the spectral region 2530–3100 A. The S_2 molecule has a very extensive system of fairly equally spaced bands with heads degraded to the red. They are mostly interspersed with the spectra of SO, so that their measurement is rather difficult. Some of the S_2 bands are shown in Figs. 4(a) and (b) and tabulated in Table I.

S_2 appears early in the explosion and attains a maximum intensity of absorption some milliseconds after the peak of the radiation curve. Its concentration decreases rapidly as the intensity of the radiation approaches zero.

Sulfur Monoxide (Monomer), SO

These studies have resulted in the first recorded absorption spectra of the sulfur monoxide monomer, SO. Many of the bands can be seen in Figs. 4(a)–(c). The wavelengths and numbers of several band heads, and of the rotational fine structure of the (1,4) band, are listed in Table II. These measurements agree closely with those obtained in emission spectra by both E. V. Martin,[7] and V. Henri and F. Wolff.[8] Previous attempts to prepare and observe SO in absorption studies have been unsuccessful because of formation of the dimer, and spectral interference by other species as discussed by N. M. Emanuel.[9] Therefore, there has been considerable uncertainty as to whether the lower electronic

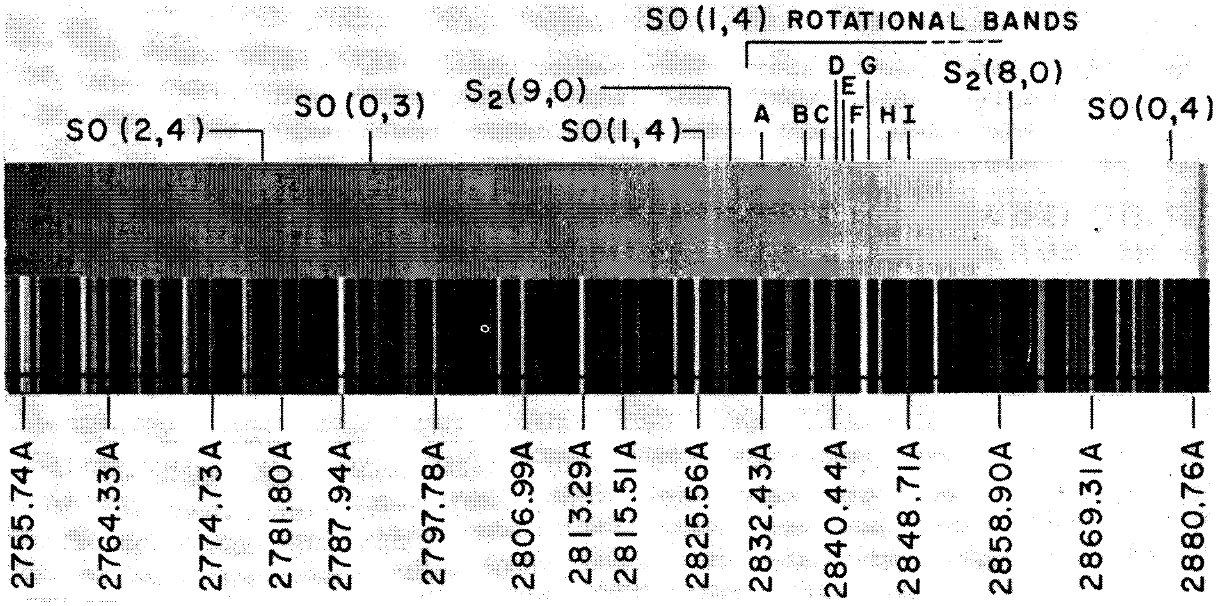

Fig. 4.(b) Absorption spectrogram of CS_2-O_2 explosion, 2756–2880 A.

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[7] E. V. Martin, Phys. Rev. **41**, 167 (1932).

[8] V. Henri and F. Wolff, J. phys. radium **10**, 81 (1929).

[9] N. M. Emanuel, Compt. rend. acad. sci. U.R.S.S. **35**, 145 (1942).

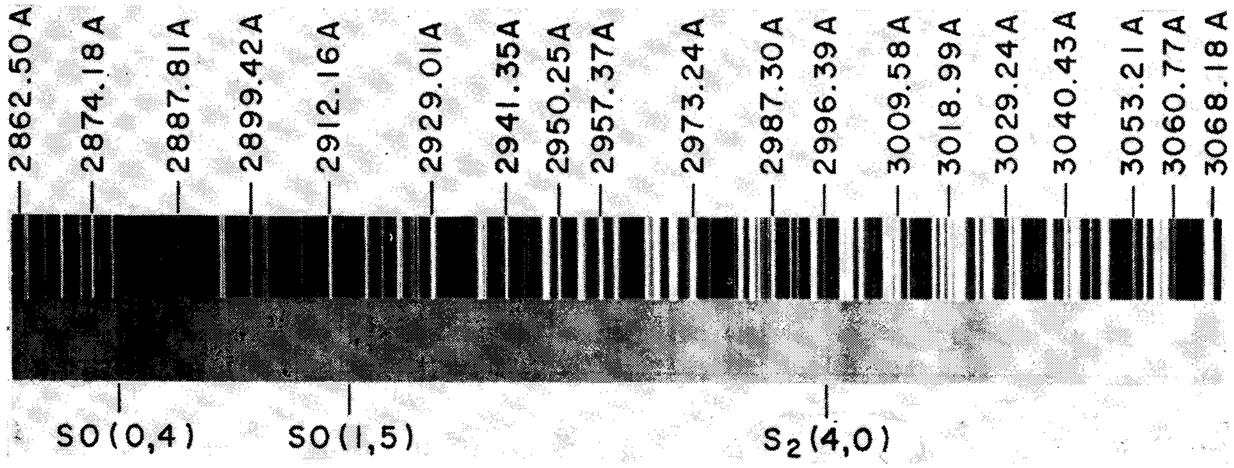

FIG. 4(c). Absorption spectrogram of CS_2-O_2 explosion, 2862–3068 A.

state $^3\Sigma$ observed in emission is the ground state.[10] It can now be concluded that $^3\Sigma$ is the ground state.

As will be noted in Figs. 4(a)–(c) SO has been observed in excited vibration levels as high as $v''=7$ (not listed in Table II). The relative intensities in the various levels do not appear to be obviously different from those expected of normal thermal distribution at the explosion temperature. In the case of the peak of the explosion, assuming the products to be CO_2 and SO_2, the calculated adiabatic flame temperatures are approximately 3720°K for 1:3 mixtures, and 3250°K for 1:6 mixtures. However, as will be explained later, there are reasons for believing that the oxide of sulfur which is present during the explosion is one of energy content lower than that of SO_2. If, for the sake of calculation, we assume the enthalpy of this product to be 30 000 calories per mole less than that of SO_2, the adiabatic flame temperatures become 3200°K and 2840°K, respectively. The relative populations calculated for levels 0 through 7 at 3200°K are 1.0, 0.61, 0.37, 0.23, 0.14, 0.09, 0.05, and 0.035, respectively. The number of molecules in the $v''=7$ level represents 1.4% of the total SO population. In the case of 1:6 mixtures (not shown), the $v''=7$ band is barely visible. This is in agreement with the calculated expectation that less than 1% of a total SO population, which is considerably less than the SO population in a 1:3 mixture, will be in this $v''=7$ level. It has been found that the absorption spectra of SO is, in all cases, less intense with increasing proportions of oxygen. The significance of this will be pointed out later in this article. The absorption of SO radicals seems to reach its maximum a short time after the peak of the radiation emission is attained, and decreases approximately in phase with the emission curve.

TABLE I. Identification of the bands of the sulfur molecule, S_2.

Observed wavelength (A)	Literature[a] wavelength (A)	Vibrational quantum numbers (v',v'')
2996.6	2996.8	4, 0
2960.0	2959.9	5, 0
2860.3	2860.0	8, 0
2829.1	2829.1	9, 0
2798.6	2798.8	10, 0

[a] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (John Wiley and Sons, Inc., New York, 1950), p. 212.

Sulfur Monoxide (Dimer), S_2O_2

Absorption bands of S_2O_2 have been observed in both exploding and heated nonexploding mixtures of CS_2-O_2. A spectrogram obtained during the early

TABLE II. Identification of vibrational bands and rotational fine structure of the sulfur monoxide monomer, SO.

Observed wavelength (A)	Literature[a] wavelength (A)	Vibrational quantum numbers (v', v'')
2510.2	2510.4	3, 1
2548.6	2548.6	2, 1
2630.0	2630.1	0, 1
2664.9	2664.8	1, 2
2699.2	2699.1	2, 3
2708.8	2708.6	0, 2
2744.2	2744.0	1, 3
2779.8	2779.8	2, 4
2791.5	2791.3	0, 3
2827.6	2827.4	1, 4
2877.9	2877.7	0, 4
2915.5	2915.4	1, 5

Some rotational lines of the (1, 4) band of SO

Line[b]	Observed wavelength (A)	Observed wave number (cm^{-1})	Literature[c] wave number
A	2832.9	35 299.5	35 299.5
B	2837.8	35 238.6	35 238.0
C	2839.4	35 218.7	35 218.2
D	2841.0	35 198.9	35 197.4
E	2842.2	35 184.0	35 186.0
F	2842.8	35 176.6	35 175.1
G	2844.8	35 151.8	35 150.3
H	2847.0	35 124.7	35 123.7
I	2849.2	35 097.6	35 097.0

[a] See reference a in Table I.
[b] See Fig. 4(a).
[c] See reference 7.

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[10] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1953), p. 573.

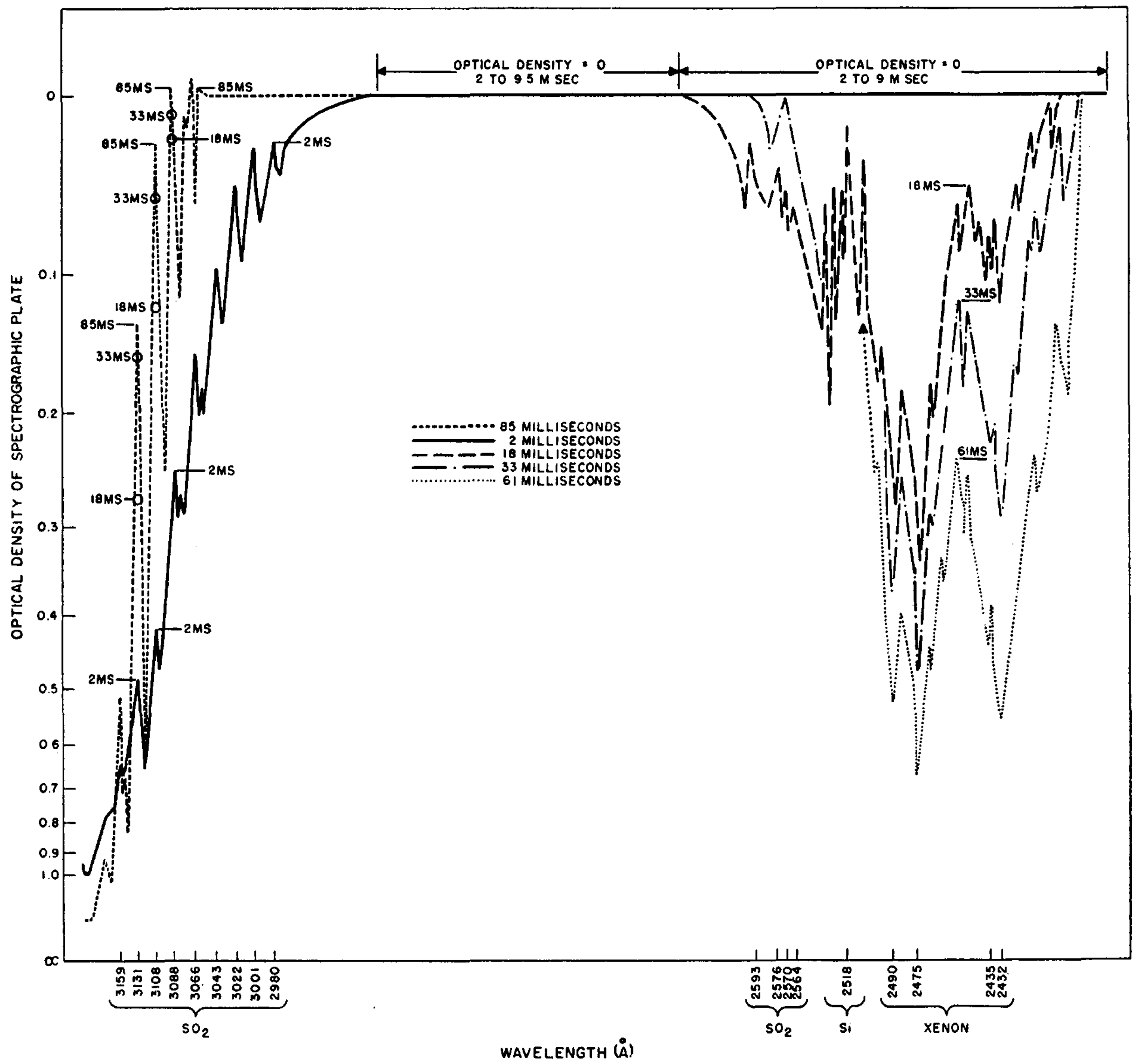

FIG. 5. Microphotometer traces of absorption spectra taken 2 to 85 milliseconds after the end of the light emission from 1:3 CS_2:O_2 explosions (total pressure=35 mm Hg). Spectra in the short wavelength region show the waning of continuous absorber. Spectra in the long wavelength region show the concurrent growth of SO_2, with complete spectra at 2 and 85 msec, and peak absorption intensities at two intermediate times for the three strongest SO_2 bands. As the SO_2 concentration increases, it is the strong absorption of SO_2 which removes the source continuum in the intermediate wavelength region.

part of an explosion of a 1:3 mixture of CS_2:O_2 ($p_{CS_2}=8$ mm Hg) displayed bands at measured wavelengths of 2972.7, 2939.9, 2907.8, and 2877.3 A. These values are in excellent agreement with those reported for S_2O_2 by H. Cordes and P. W. Schenk,[11] by N. M. Emanuel, D. S. Pavlov, and N. N. Semenov,[12] and others.[13] These spectra were originally discovered by Cordes and Schenk and at first mistaken for a metastable system of S_2 by Cordes.

The S_2O_2 molecules were also detected, through these same bands, in a nonexploding 1:3 mixture of CS_2:O_2, at 121°C and 25 mm Hg. Red crystals were obtained by quickly condensing mixtures of this type at liquid nitrogen temperatures. These crystals undoubtedly correspond to the red crystals of S_2O_2 reported by Cordes and Schenk,[11,14] and others.

Sulfur Dioxide, SO_2

The absorption due to SO_2 is surprisingly weak during the explosion. This was concluded from a comparison of the explosion spectra with spectra obtained from explosions of mixtures to which known amounts

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[11] H. Cordes and P. W. Schenk, Z. Elektrochem. **39**, 594 (1933).

[12] Emanuel, Pavlov, and Semenov, Compt. rend. acad. sci. U.R.S.S. **28**, 7, 618 (1940).

[13] A. Vallance Jones, J. Chem. Phys. **18**, 1263 (1950).

[14] P. W. Schenk, Chem. Ztg. **20**, 251 (1943); **21**, 273 (1943).

of SO_2 had been added. This point will be discussed more fully in the next section. In all cases, the concentration of SO_2 during and at the end of the explosion never exceeds more than a few percent of its final stoichiometric concentration. Equally conspicuous is the slow and very interesting formation of SO_2 to its final, and nearly stoichiometric concentration after the explosion, as can be seen in Fig. 5. The final spectrum was taken 85 msec after the cessation of an explosion of a 1:3 CS_2:O_2 mixture. The absorption bands indicate the presence of the order of 6 mm of Hg of normal SO_2. Complete reaction would have produced 16 mm Hg of SO_2. A series of spectra obtained after a 1:6 explosion show similar results, with approximately 3 mm Hg of SO_2 present after 28 msec.

The Absorption Continuum

A strong absorption continuum is apparent in all ultraviolet spectra taken during CS_2-O_2 and $COS-O_2$ explosions. The absorption coefficient of the species responsible appears to be greatest at the shortest wavelengths observed or 2100 A, and to decrease with increasing wavelength at least to 3100 A. Thus, as the explosion proceeds, the region of continuous absorption extends to longer wavelengths. This can be seen in the spectra represented by the microdensitometer traces of Fig. 6, in which the long wavelength limit of absorption increases from 2430 to 2976 A in a period of 10 msec during the explosion.

Comparison of exploding 1:3 and 1:6 CS_2:O_2 mixtures has shown that increasing the partial pressure of O_2 increases the intensity of the absorption by the continuous absorber.

The absorption intensity of the continuous absorber reaches its maximum at the end of the explosion. The spectroscopic disappearance of the continuous absorber after the explosion is shown kinetically in Fig. 5. This gradual waning of the absorbing species can be seen to coincide with the growth of SO_2 from its initial (small) concentration at the end of the explosion to its final (high) concentration. It should be noted that as the SO_2 concentration increases, it is the strong absorption of SO_2 which removes the source continuum from 2500 to 3050 A.

The obvious possibility that the absorption continuum is the high-temperature spectrum of SO_2 was eliminated early in our considerations because of numerous observations. The most important of these are:

(1) A series of spectra was obtained during explosions of mixtures to which varying amounts of SO_2 had been added. Even when as little as 2 mm Hg of SO_2 were added to mixtures containing 8 mm Hg of CS_2, a very significant increase in the intensity of the characteristic 2500–3000 A system of SO_2 could be noted at the peak of the explosion, over the weak intensity in the corresponding spectra of a mixture to which no SO_2 had been added and in which 16 mm Hg of SO_2 are eventually formed. If at the peak temperature, the intensity of these bands arising from 16 mm Hg of SO_2 is decreased by the observed 95% or so because of temperature, the same decrease should be true for the spectral intensity of the 2 mm Hg of SO_2 which were added. We would expect an increase of only 2/16, or 13%, over the intensity observed without SO_2 addition. Actually, the increase in the intensity of the SO_2 absorption bands resulting from the SO_2 addition is several hundred percent.

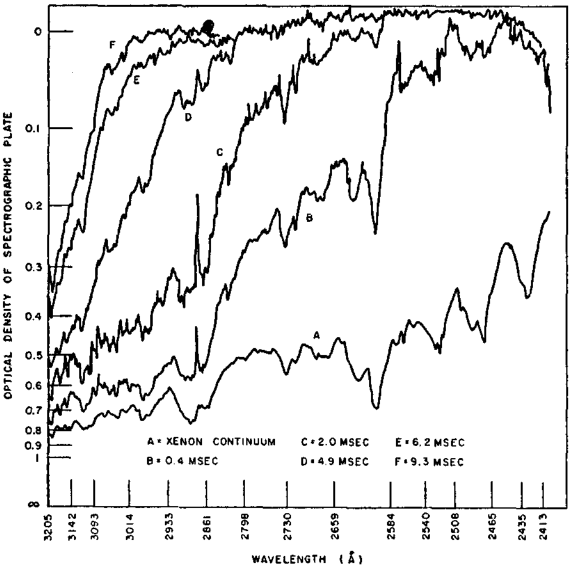

Fig. 6. Microphotometer traces of absorption spectra showing growth of continuous absorber during 1:3 CS_2:O_2 explosions (total pressure = 35 mm Hg). The time, in milliseconds, after the beginning of light emission at which each spectrum was taken is given by *B* through *F*.

(2) The continuous absorption is weakened rather than strengthened by addition of even 2 mm Hg of SO_2.

(3) The intensity of the continuous absorption continues to increase for 6 msec or so after the peak (temperature) of the explosion has been reached. If this were a true temperature effect, the continuum would begin its regression as soon as the temperature began to fall.

(4) The SO_2 spectra (2500–3000 A system) visible even at highest temperatures appears to be little changed from the reaction temperature (200–300°C) spectra, under the resolution of our spectrograph. The fine structure of the bands is probably more diffuse and the lines broadened but their position is the same. The observed transition from continuous absorber to SO_2 is definitely an either—or proposition; that is, the absorption is either that characteristic of the described bands at 2500–3000 A, or else the continuum with a maximum intensity below 2000 A. There is no evidence of gradual broadening of the bands themselves, which would be expected in a temperature effect.

(5) The continuous absorber is more intense with 1:6 CS_2:O_2 mixtures than with 1:3 CS_2:O_2 mixtures

at corresponding times in the explosion process. Since flame temperatures of 1:6 mixtures are cooler, by 400°C or more, than those of 1:3 mixtures, a theory of temperature effect would not fit these observations.

(6) What appears to be the same absorption continuum has been observed at higher pressures in nonexploding mixtures at furnace temperatures (i.e., 200–300°C).

That the continuous absorption is due to electronically or vibrationally excited SO_2 must be considered. However a comparatively long time, of the order of tenths of a second, is required for the complete replacement of the continuous absorber by normal SO_2. At pressures of 40 to 60 mm Hg, where a given molecule encounters 10^9 collisions per second, even the most inefficient physical quenching of electronic, vibrational or rotational excitation, which might require 10^4 or 10^5 collisions, cannot explain the comparative stability of the continuous absorber.

The absorption coefficient of this unknown absorber varies with wavelength very much as do the coefficients of sulfur trioxide (SO_3)[15] and ozone (O_3).[16] Reference spectra indicated that impossibly high concentrations of SO_3 would be necessary to account for any significant portion of the absorption observed. In the case of ozone, reference spectra showed that 8 mm Hg of O_3 would be necessary to absorb to the observed limit of 3000 A. Furthermore, continuous absorption has been observed to 3150 A, which would require the formation of almost 14 mm of Hg of ozone, in an explosion of 8 mm of CS_2 and 24 mm of O_2. Thus O_3 cannot be responsible for more than a small fraction of the continuous absorption. Ozone is formed via three-body collisions ($O+O_2+M$) which, under these conditions, are undergone by a given oxygen atom 10^3 times per sec, compared to the corresponding two-body process of 10^9 per sec.

IV. ADDITIONAL RESULTS AND DISCUSSION OF THE CHEMICAL MECHANISM

It is convenient to consider the combustion process chronologically, in terms of three phases which overlap in time: (A) the initial production of chain carriers; (B) the induction period and chain branching propagation; (C) the explosion and after.

A. The Initial Production of Chain Carriers

Studies[17–19] of the ignition limits of CS_2-O_2 mixtures have shown that the explosions occur through a chain branching mechanism which is extremely sensitive to the vessel surface. Further, it has been shown[20] that the reactions of the induction period which lead to explosion depend on chain initiation in the gas phase and chain destruction at the (vessel) wall. These latter conclusions were drawn from observations on the effect of flask size and surface upon reaction rates and ignition limits. In determining the gas phase reaction(s) responsible for the initial formation of free radicals, several possibilities can be eliminated by virtue of the very low temperatures at which thermal explosion can be observed (<75°C), and at which a slow reaction is readily discernible. At 140°C and 50 mm Hg pressure, it was found spectroscopically that a 1:3 mixture of $CS_2:O_2$ produces several mm of Hg of SO_2 per hour. Let us consider the direct thermal dissociation of the reactants as the source of chain carriers producing SO_2 (see W. Lochte-Holtgreven and C. E. H. Bawn for $\Delta H_{(1)}{}^{21}$):

$$CS_2 \rightarrow CS+S-101\text{ kcal,} \qquad (1)$$

$$O_2 \rightarrow O+O-117\text{ kcal.} \qquad (2)$$

It can be readily calculated, from these dissociation energies that inconceivably long chains would be required for either (1) or (2) to produce SO_2 at the rate measured.

However our experiments showed that CS is immediately apparent in mixtures of CS_2 and O_2 at temperatures as low as 50°C. As previously noted, this occurs along with the formation of SO_2. A bimolecular gas phase reaction between CS_2 and O_2 remains as an excellent possibility for the initiating process. If the immediate product were sulfur dioxide which, as will be seen later, is not the case, the reaction would be decidedly exothermic:

$$CS_2+O_2 \rightarrow CS+SO_2+36\text{ kcal.} \qquad (3)$$

It is necessary, however, to make an important change in (3) to render it compatible with the facts. As written, (3) could not be responsible for a chain reaction[22] leading to an explosion, or even to a slow reaction. CS has been shown to be stable to oxidation by O_2 up to temperatures of 100°C.[18,23] Since one product of (3) is definitely CS, at least one of the other products must be an active center or capable of producing one. It can be readily concluded that the reaction of CS_2 and O_2 to produce, directly, $CS+SO+O$ is energetically impossible. Nor have we detected other reactive species as SO or S_2, in heated mixtures. Whether the reaction first takes place through an

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[15] E. Fajans and C. F. Goodeve, Trans. Faraday Soc. **32**, 511 (1936).

[16] A. Laüchli, Helv. Phys. Acta **1**, 208 (1928).

[17] N. Semenoff, *Chemical Kinetics and Chain Reactions* (Clarenden Press, Oxford, 1935), p. 280.

[18] H. W. Thompson and C. F. Kearton, Z. physik. Chem. **14B**, 359 (1931).

[19] A. L. Myerson and F. R. Taylor, J. Am. Chem. Soc. **75**, 4348 (1953).

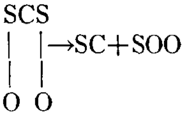
[20] Myerson, Taylor, and Trevathan, Franklin Institute Laboratories, Final Technical Report 54-377 to Wright Air Development Center, Contract No. AF 33(038)-20863, October, 1954.

[21] W. Lochte-Holtgreven and C. E. H. Bawn, Trans. Faraday Soc. **28**, 698 (1932).

[22] A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (John Wiley and Sons, Inc., New York, 1953), Chap. 10.

[23] V. Kondratyev and E. Magaziner, Zhur. Fiz. Khim. **14**, 1, 609 (1940).

unstable cyclic complex



$$\begin{array}{l}\mathrm{SCS}\\ |\;\;| \rightarrow \mathrm{SC}+\mathrm{SOO}\\ |\;\;|\\ \mathrm{O}\;\mathrm{O}\end{array} \qquad (4)$$

or through sulfur abstraction, the other product must be a sulfur superoxide, SOO, analogous in structure to ozone.

Although it would be expected that (3) is more exothermic than (4), and hence has a smaller energy of activation, the rate of (4) should be favored to a considerable extent over the rate of (3) by a much more positive entropy of activation. Reaction (3) produces the products CS+OSO where the O_2 bonding must be completely rearranged. This conclusion regarding the formation of SOO is strongly supported by our discovery, in hot nonexploding mixtures, of the same continuous absorbing species observed (see Sec. III) during the explosion. Its concentration increases with the pressure of the heated CS_2-O_2 mixture, and its absorption coefficient in the uv is approximately the same function of wavelength as is the absorption coefficient of ozone. This is reasonable to expect for a species which differs from ozone, OOO, by the substitution of an end S atom. Evidence that the continuous absorber observed during the explosion also is SOO will be presented later in this article.

Applying the theory of superoxide formation to $COS-O_2$ explosions which were studied briefly, one would expect as products CO and SOO but not CS (the energy of the CS bond in COS is 76 kcal per mole; that of the CO bond is 148 kcal[21]). As previously stated, CS was absent from COS explosions, while the continuous absorber was as strong as in the CS_2 explosions.

The mechanism by which chains are initiated by sulfur superoxide, SOO, depends on the stability and reactivity of this molecule. Calculations have been made in order to construct potential energy surfaces for the system SOO by means of the Eyring semi-empirical treatment of the Heitler-London theory.[24] While the results of such work do not constitute irrefutable evidence, it is interesting to note that the calculations do indicate that SOO is stable.

Thermochemical considerations, however, require that SOO be less stable than SO_2 by a significant margin if chains are to be produced through the superoxide. There are two reasonable paths by which chain carriers can be produced under those circumstances. Although the direct decomposition of SOO probably would produce free radicals, there is a route to branching and explosions which seems to be clearly indicated. This path is through the formation of S_2O_2. This mechanism may be deduced from three experimental observations: (a) spectroscopic identification of S_2O_2 in the very early stages of the explosion; (b) observation of the characteristic pink-red crystals of S_2O_2 in the otherwise pure white condensate of heated unexploded mixtures of CS_2-O_2; (c) the chemical properties of S_2O_2 as determined by previous investigators.

The most obvious mechanism for its formation would, at first thought, appear to be through the reaction postulated by P. W. Schenk[14] and others,

$$S+SO_2 \rightarrow S_2O_2 \qquad (5a)$$

and in our case

$$S+SOO \rightarrow S_2O_2. \qquad (5b)$$

However, S_2O_2 is present only during the induction period and very early stages of the explosion. It is doubtful that the concentration of both SO_2 (and/or SOO) and sulfur atoms is sufficient at these times for these bimolecular reactions to be at all important. Much more likely is the reaction of SOO with one of the original reactants

$$CS_2+SOO \rightarrow CS+S_2O_2. \qquad (6)$$

From the spectroscopic studies of the conversion of SOO to SO_2, it is apparent that the lifetime of SOO is long enough for reactions such as (6) to take place. The accumulation of S_2O_2 in itself can lead to ignition. H. Kondratyeva, E. Kondrateva, and V. Kondratyev[25,26] showed that $S_2O_2-O_2$ mixtures containing only 0.5 mm Hg of S_2O_2 exploded at temperatures as low as 55°C under circumstances characteristic of a chain mechanism.

In the absence of reactive species it would be expected that SOO effectively rearranges to the more stable SO_2:

$$SOO \rightarrow SO_2+\text{energy}. \qquad (7)$$

This will be discussed subsequently.

B. The Induction Period and Chain Branching Propagation

1. *The Role of SO*

Identification of SO in a high steady-state concentration throughout the explosion is indicative of its important role as a chain carrier and serves to clarify current concepts of the reactivity of the sulfur monoxide monomer. An article typical of several written in the thirties[27] stated that sulfur monoxide is extremely nonreactive to oxygen. It was shown subsequently[13,26,28a,28b] that the spectrum originally ascribed to sulfur monoxide (monomer) is actually that of S_2O_2, which does react slowly enough with O_2 at temperatures and pressures below the ignition limits. It was deduced in the works

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[24] Glasstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

[25] H. Kondratyeva and V. Kondratyev, Compt. rend. acad. sci. U.R.S.S. **31**, 2, 128 (1941) (in English).

[26] E. Kondratyeva and V. Kondratyev, Zhur. Fiz. Khim. **18**, No. 3–4, 102 (1944). (English translation by Assoc. Tech. Services, No. 25F3R.)

[27] H. Cordes and P. Schenk, Z. anorg. allgem. Chem. **214**, 33 (1933).

[28] (a) A. Jakovleva and V. Kondratyev, Acta Physicohim. U.R.S.S. **13**, 241 (1940); (b) N. M. Emanuel, Compt. rend. acad. sci. U.R.S.S. **36**, No. 4–5, 145 (1942) (in English).

cited,[26,28b] and is now effectively proved for the first time from the present research that the species SO in its ground state is a principal chain carrier in explosions of the mixtures $S_2O_2-O_2$, CS_2-O_2 and H_2S-O_2.

Also relevant to these considerations is the conclusion of V. Kondratyev *et al.*[29,30] that SO is completely dimerized to S_2O_2 at lower temperatures and that

$$S_2O_2 \rightarrow 2\,SO - 49.5\text{ kcal}, \tag{8}$$

although another group[30a] has reported evidence, through pressure measurements only, of incomplete dimerization of S_2O_2 at low pressures (*ca* 1 mm Hg). The former workers[29,30] also showed that $\Delta H(5a)=12$ kcal, which strongly indicates that the reverse of (5a) is the reaction responsible for the initiation of chains from accumulated S_2O_2.

The inclusion of the reactions

$$SO+O_2 \rightarrow OSO+O+18\text{ kcal}, \tag{9a}$$

$$SO+O_2 \rightarrow SOO+O, \tag{9b}$$

as the principal propagating reactions of SO, presents a number of mechanistic difficulties. This matter may be more clearly discussed by considering separately the reactions occurring at: (a) the low temperatures existent during the induction period and early stages of the reaction; and (b) the high temperatures of the explosion.

During the low temperatures of the induction period (i.e., as low as 75°C), it is likely that the activation energy of (9a), and hence (9b) as will be shown later, is too large to permit propagation at the rates observed. Accurate calculations of E^* (9a) involve the difficulties encountered in the previously mentioned calculations of SOO. However, in view of the observed free radical behavior of SO, including its $^3\Sigma$ ground state and its strong tendency to dimerize ($\Delta H=-40$ to -50 kcal/mole; compare O_2 and O_4), it is probable that E^* (9a) is not too much greater than (e.g., twice) the 7 kcal or less we might expect if SO were a monatomic free radical. Whether the activation energy is one compatible with the rates observed is problematical, but there does exist a logical possibility for a scheme which would continue the chain through steps of lower energies of activation.

Now there can be no question that the highly reactive SO will react with O_2 to form the relatively stable sulfur trioxide, SO_3:

$$SO+O_2 \rightarrow SO_3+100\text{ kcal}. \tag{10a}$$

This oxide is found in considerable amounts in the products of the oxidation of CS_2 and similar sulfur compounds.[25,26] It is generally assumed that SO_3 has the symmetrical structure

$$\begin{matrix} & O & \\ & S & \\ O & & O. \end{matrix}$$

However, it would be supposed that the initial formation of the activated complex would involve the unbroken O—O bond:

$$SO+O_2 \rightarrow OOSO, \tag{10b}$$

$$SO+O_2 \rightarrow SOOO. \tag{10c}$$

What seem to be reasonable results have been obtained for semiempirical potential energy calculations for configurations along the reaction coordinate from infinite separation of SO and O_2 to the point of maximum potential energy of linear forms of SOOO and OSOO. Using 25% Coulombic energy, an activation energy of 7 or 8 kcal results for (10b) or (10c). The depth of the energy well for the product is of the same order of magnitude (i.e., $\Delta H=0$). It is then not difficult to conceive of reactions of low activation energies taking place between these highly oxygenated products and reducing radicals and molecules, as well as between SO_3 and reducing species.

The reactions of SO during the much higher temperatures of the explosion will be considered in the last part of this article.

2. *Reactions of the Oxygen Atom*

Three sets of products are stoichiometrically possible as a result of the reaction of an O atom with CS_2:

$$CS_2+O \rightarrow CS+SO+19\text{ kcal}, \tag{11}$$

$$CS_2+O \rightarrow COS+S+47\text{ kcal}, \tag{12}$$

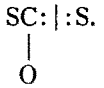
$$CS_2+O \rightarrow CO+S_2+70\text{ kcal}. \tag{13}$$

P. Harteck and U. Kopsch actually observed[31] the rapid reaction of O atoms with CS_2, using O atoms created by an electrical discharge. The final products were SO_2, SO_3, CO, CO_2, and sulfur.

All three of these reactions obey the Wigner-Witmer spin correlation rules. However, on the basis of activation energies there are reasonable grounds for concluding that (12) is the most rapid reaction of the three.

In the case of (13) the breaking of *two* CS bonds requires a total energy of 267 kcal per mole. Thus (13) would be slow compared to (11) and (12) where in both cases only one CS bond is ruptured. Further comparison of (11) and (12) shows that the breaking of one and the same CS bond of CS_2 is involved:

$$SC{:}\,|\,{:}S-O \tag{11}$$



$$\begin{matrix} SC{:}\,|\,{:}S. \\ | \\ O \end{matrix} \tag{12}$$

However, in (11) the energy of the SO bond formed is 119.5 kcal per mole while in (12) that of the CO bond of SCO is 148 kcal/mole. This difference should result in a significantly lower activation energy for (12). The

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[29] V. Kondratyev and A. Yakovleva, Zhur. Fiz. Khim. **14**, 859 (1940).

[30] E. Kondratyeva and V. Kondratyev, Zhur. Fiz. Khim. **14**, 1528 (1940).

[30a] Evans, Scott, and Huston, J. Am. Chem. Soc. **74**, 5525 (1952).

[31] P. Harteck and U. Kopsch, Z. physik. Chem. **B12**, 327 (1931).

only other factor[32] that might be important is the repulsion energy of approach, which could hardly disfavor (12) by as much as 28 000 cal/mole.

COS, although thermally quite stable, cannot attain a very high concentration since it, like CS_2, is susceptible to attack by oxygen atoms. Mixtures of COS and oxygen explode at only slightly higher temperatures than do those of CS_2 and oxygen. Unfortunately, COS could not be detected during the CS_2-O_2 explosion because of its continuous absorption spectrum in the uv. However, we have also studied the flash absorption spectra of $COS-O_2$ explosions. These experiments have provided information which is in line with the premise that COS undergoes reactions analogous to (11) and (12):

$$COS+O \rightarrow CO+SO+43 \text{ kcal}, \qquad (14)$$

$$COS+O \rightarrow CO_2+S+51 \text{ kcal}. \qquad (15)$$

If we add to our scheme the reaction

$$COS+O_2 \rightarrow CO+SOO \qquad (16)$$

then reactions (14), (15), and (16) may be considered to be the COS counterparts of the CS_2 reactions (11), (12), and (4). Thus CS should appear in CS_2-O_2 explosions but not in $COS-O_2$ explosions. Spectra of all COS explosions which we have observed clearly verify the absence of CS.

3. *The Sulfur Atom, S*

Until recently, the dissociation energy of SO has been unresolved with respect to two values of 92 and 119.5 kcal per mole. A recent study[33] of the thermal dissociation of SO_2 concludes that the higher value is correct. This high value for the bond energy of SO, our spectroscopic identification of SO as an important intermediate, and the strongly indicated production of sulfur atoms through reactions (12) and (15) all lend credence to the important participation of reaction (17) in CS_2-O_2 explosions:

$$\overset{^3P}{S}+\overset{^3\Sigma}{O_2} \rightarrow \overset{^3\Sigma}{SO}+\overset{^3P}{O}+2.5 \text{ kcal}. \qquad (17)$$

It will be noted that the reaction is exothermic, fulfills the requirements of the Wigner-Witmer spin correlation rules, and involves the ^3P sulfur atom which is produced by reactions (12) and (15). It can be assumed, therefore, that the activation energy is small, or not more than 5 or so kcal per mole.

Since SO is a chain carrier, the reaction is responsible for chain branching. As a matter of fact, it is apparently the only reaction which can be considered capable of providing the branching necessary for explosion at the ignition temperatures observed.

Reaction (17), by virtue of its being primarily responsible for chain branching also serves as an explanation for the second limit. At the higher pressures of the second limit, collisions involving another molecule capable of carrying off any considerable amount of energy make reactions (18a) and (18b) possible:

$$S+O_2+M \rightarrow SO_2^*+M^* \qquad (18a)$$

$$S+O_2+M \rightarrow SOO^*+M^*. \qquad (18b)$$

C. The Explosion and After

1. *Species Responsible for the Absorption Continuum*

The facts established in these studies have indicated a rather unexpected turn regarding the identity of the principal and final oxide of sulfur formed *during* the explosion. It has been necessary to conclude that it is not sulfur dioxide but rather an isomer, SOO. which yields the more stable SO_2 on cooling.

In reaching this conclusion, the following observations and deductions which include a review of those in previous sections, are important.

(a) At the end of the explosion, the partial pressure of SO_2 is only of the order of 1 or 2 mm of Hg, where a stoichiometric pressure of almost 16 mm Hg is expected. This is based on the SO_2 spectrum at explosion temperatures. The possibility that the continuous absorption is due to electronically or vibrationally excited SO_2, or is only its high temperature spectrum, can be eliminated for the reasons fully discussed in Sec. III under "The Absorption Continuum."

(b) By the end of the explosion, the species which absorbs in a continuum has steadily accumulated or increased from zero to its maximum concentration causing strong continuous absorption to wavelengths as long as 3000 A. Since other intermediates such as SO and S_2 have faded away by this time, it is impossible that the SO_2 is being formed after the explosion from recombination of these intermediates.

(c) Spectra taken after the explosion, as presented, show that as the continuous absorption decreases in intensity the SO_2 begins to appear as illustrated by Fig. 6.

Therefore, the species principally responsible for the continuous absorption is either a direct precursor of SO_2 or a molecule which reacts, as the gases cool, with other final products to produce SO_2. The only possibilities for a molecule with an absorption spectrum as described, among the known molecular species in this chemical system, are SO_3 and O_3. Both of these can be eliminated as being solely or even principally responsible, for spectroscopic and chemical reasons previously discussed.

With the elimination of the possibilities cited, it must be concluded that this absorption is due to a direct and unknown precursor of SO_2. This precursor would have to possess an absorption spectrum similar to that of ozone. An isomeric form of SO_2, namely SOO,

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[32] K. J. Laidler, *Chemical Kinetics* (McGraw-Hill Book Company, Inc., New York, 1950), Chap. 13.

[33] G. St. Pierre and J. Chipman, J. Am. Chem. Soc. **76**, 4787 (1954).

should be considered. This molecule would be expected to possess chemical bonding similar to that of both ozone and sulfur dioxide. Estimates of the bond energies have already been mentioned. It was concluded that it must be considerably less stable than SO_2, so that a bimolecular or chain rearrangement to the latter would be expected.

2. *Factors Responsible for the Small Ratio of SO_2 to Continuous Absorber (SOO) during the Explosion*

Although the SO_2 spectrum is very weak during the explosion, energetic considerations make it unlikely that the rate of

$$SO+O_2 \rightarrow SO_2+O \qquad (9a)$$

is significantly slower than the rate at which the same reactants would produce SOO [reaction (9b)]. However, oxidation of SO may proceed through the intermediate formation of SO_3 and its isomers [reactions (10a), (10b), and (10c)]. Then the rate of formation of SOO by reduction of isomers of SO_3 is favored over the rate of formation of SO_2 by a ratio of roughly 3:1 on a statistical basis. This follows because all SOOO molecules, and perhaps half of those of OSOO, would produce SOO.

There are two other factors which are very important in explaining the weak SO_2 spectra: First, as the temperature of the gases increases, the relative importance of nonfree radical or molecular reactions becomes greater. Thus by the time the temperature has reached 1700°K (peak temperature for a 1:3 explosion is perhaps 3200°K), reactions such as

$$COS+O_2 \rightarrow CO+SOO \qquad (19)$$

and (4) may well be significant. The energy of the CS bond in COS, the primary product from the initial oxidation of CS_2 [reaction (12)], is only 76 kcal per mole, and the reaction is without doubt exothermic. It is thus likely that the activation energy is not more than 20 kcal per mole. Let us assume $E^* = 24\,000$ kcal per mole, a frequency factor of 10^{13}, a pressure of 15 mm of Hg of O_2, a steady-state partial pressure of 1 mm Hg of COS and a temperature of 1500°C. Under these conditions, 0.5 mm Hg of COS will react in one millisecond.

Second, the partial pressure of SO_2 during the explosion is limited by the reaction of SO_2 with an oxygen atom

$$SO_2+O \rightarrow SO_3+81 \text{ kcal}. \qquad (20)$$

Evidence for this reaction with an activation energy of approximately 6 kcal, has been presented by G. Whittingham[34] who was able to conclude that SO_3 can be formed in $CO-O_2$ flames to which SO_2 has been added. The analogous reaction of SOO with an oxygen atom would not be expected to proceed at a rate comparable with (20). This follows from the great stability of SO_3, compared to that of the product of SOO+O.

V. SUMMARY OF THE PRINCIPAL REACTIONS OF THE PROPOSED MECHANISM

Initiation:

$$CS_2+O_2 \rightarrow CS+SOO, \qquad (4)$$

$$CS_2+SOO \rightarrow CS+S_2O_2, \qquad (6)$$

$$S_2O_2 \rightarrow S+SO_2. \qquad (5a)$$

The induction period and chain branching propagation:

$$S+O_2 \rightarrow SO+O, \qquad (17)$$

$$CS_2+O \rightarrow COS+S, \qquad (12)$$

$$\left.\begin{aligned} SO+O_2 &\rightarrow OOSO \\ SO+O_2 &\rightarrow SOOO \end{aligned}\right\} \begin{aligned} &\text{continue chains} \qquad (10b) \\ &\text{through oxidation,} \qquad (10c) \end{aligned}$$

$$SO+O_2 \rightarrow SO_3, \qquad (10a)$$

$$COS+O \rightarrow CO_2+S. \qquad (15)$$

Additional reactions at explosion temperatures significantly above those of initial reactions:

$$COS+O_2 \rightarrow CO+SOO, \qquad (16)$$

$$SO+O_2 \rightarrow SO_2+O, \qquad (9a)$$

$$SO+O_2 \rightarrow SOO+O, \qquad (9b)$$

$$SO_2+O \rightarrow SO_3. \qquad (20)$$

The post-explosion period:

SOO→OSO (mechanism not postulated). (7)

ACKNOWLEDGMENTS

The authors wish to thank the following: Dr. Keith J. Laidler and Dr. D. A. Ramsay for reading the manuscript and for their helpful suggestions; Mr. John H. Kratz for his effective design of the electronic apparatus; and Mr. Karl Scheller for his cooperation as technical representative of the Chemistry Research Branch of the Aeronautical Research Laboratories of Wright Air Development Center.

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[34] G. Whittingham, *Third Combustion Symposium* (Williams and Wilkins, Baltimore, 1949), p. 453.