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CS_2 + O_2 Self-Ignition and the Activated Complex in Its Rate-Limiting Step

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Abstract—It is demonstrated using experimental data that the elementary reaction O + CS_2 = OCS + S is a necessary step of the self-ignition of the carbon disulfide + air mixture at moderate temperatures. The structural and energetic parameters of the activated complex in this reaction are determined by quantum chemical analysis.

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Carbon disulfide is self-ignitable in air even near room temperature (see, e.g., [1]) under conditions of negligible self-heating. This suggests that carbon disulfide self-ignition is a branched chain reaction and that the activation energies of all of its chain propagation steps, including the multiplication of free valences, do not exceed 7 kcal/mol. The mechanisms of such processes remain very obscure. This is particularly true for biradical chain reactions, such as carbon disulfide combustion. In addition, there is only scanty information concerning activated complexes in low-energy-barrier elementary reactions of biradicals.

In chemical kinetic theory, carbon disulfide combustion is primarily known as the process in which so-called nonthermal flame propagation, predicted in [2], was observed for the first time [3]. The essence of this phenomenon is that, even if the composition of a mixture falls outside the self-ignition concentration range, artificial initiation of its combustion causes flame propagation requiring no reactant self-heating [4, 5]. Figure 1 presents experimental self-ignition and nonthermal flame propagation limits for the 0.03% CS_2 + air mixture [3]. Here, the absence of self-heating during combustion is due to the very low carbon disulfide concentration.

Nonthermal flame propagation is due to fast reactions between reactive intermediates, which multiply these intermediates and thus lead to chain branching [4, 5]. Since the rates of these reactions are proportional to the product of the reacting species concentrations, the chain branching that they cause is called nonlinear to reflect the nonlinearity of the reaction rate as a function of the concentrations of the intermediate products.

Free O and S atoms, $SO^{\bullet}$ and $CS^{\bullet}$ radicals, and COS molecules were identified in the rarefied carbon disulfide–oxygen flame [6–11]. The rate constants of nearly all of the main reactions in this combustion process have been determined to date [12–18]. The nonthermal flame propagation was simulated using a reaction scheme consisting of 23 elementary reactions, including various reactions between the initial species and intermediates, and a qualitative insight into the process was gained [19].

However, the self-ignition mechanism of CS_2 + O_2 mixtures has not been addressed until recently. No attention has been given to the critical self-ignition conditions [20–22]. At the same time, the nonthermal flame propagation and self-ignition regimes show different

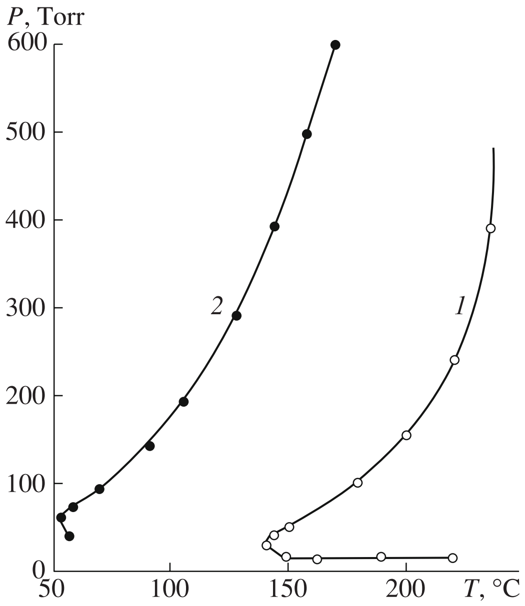

Fig. 1. Pressure limits for (*1*) self-ignition and (*2*) nonthermal flame propagation in the 0.03% CS_2 + air mixture [3].

kinetics and macrokinetics and, in addition, arise from different kinds of reactions.

Specific Features of the CS_2 Self-Ignition Mechanism

As distinct from nonthermal flame propagation, which requires that two kinds of reactive species be involved in the reactive species multiplication reaction, self-ignition requires that reactive species be multiplied via a reaction between one reactive species and the initial reactant. Since the rate of such reactions depends linearly on the concentration of reactive intermediates, they are conventionally called linear-law steps. In the reaction system considered, this nonlinear-law reaction is

$$O + CS_2 = SO^{\bullet} + CS^{\bullet}. \qquad (I)$$

However, this reaction is not the chain branching step responsible for CS_2 self-ignition at the low temperatures examined. Indeed, below 500 K, the resulting $CS^{\bullet}$ radical cannot propagate the reaction chain, because the activation energy of the reaction

$$CS^{\bullet} + O_2 = OCS + O \qquad (II)$$

is above 15 kcal/mol [14] and the rate constant, e.g., at 340 K for a mixture containing 20–30% CS_2, is as low as 2×10^6 cm^3 mol^{-1} s^{-1}. Accordingly, this reaction is so slow that it cannot compete with the $CS^{\bullet}$ decay reaction on the surface at first-limit pressures near 100 Pa. Thus, the $CS^{\bullet}$ radical is uninvolved in chain propagation, at least below 500 K. This is confirmed by experimental data indicating that $CS^{\bullet}$ is deposited on the reactor walls. Therefore, reaction (I) is only a chain propagation step in which no chain carrier multiplication takes place and the O atom replaces the $SO^{\bullet}$ radical, another reactive species. At the same time, the fact that carbon disulfide does self-ignite at these low temperatures suggests that there is a fast linear-law branching reaction. This reaction is

$$S + O_2 = SO^{\bullet} + O. \qquad (III)$$

Due to the large rate constant of the reaction

$$SO^{\bullet} + O_2 = SO_2 + O \qquad (IV)$$

both products of reaction (III)—$SO^{\bullet}$ and O—can propagate the reaction chain and thus multiply reactive species (i.e., cause chain branching).

However, it is obvious that this chain branching can obey a linear law only when the formation rate of the S atom, which multiplies free valences, is also a linear function of the concentration of reactive intermediates. The linear-law S atom formation reaction is the direct replacement of S in the CS_2 molecule:

$$O + CS_2 = OCS + S. \qquad (V)$$

The disproportionation reaction yielding an S atom,

$$SO^{\bullet} + SO^{\bullet} = SO_2 + S \qquad (VI)$$

cannot account for the observed self-ignition, because its rate depends nonlinearly on the concentration of the intermediate species $SO^{\bullet}$.

Earlier studies of reactions of hydrogen and deuterium atoms [23, 24] discovered direct homogeneous and heterogeneous substitution and displacement reactions of atoms in various multiatomic saturated molecules. It was demonstrated that these reactions are characterized by a low activation energy and a large preexponential factor. The latter is only slightly below the number of binary collisions. Heterogeneous reactions of this type make a significant contribution to combustion and plasma chemical processes [24].

Here, we report the role of reaction (V) in carbon disulfide ignition and combustion and characterize the activated complex in this elementary event. Experimental data available on the second self-ignition limit will be used. Along with an analysis of experimental data concerning carbon disulfide ignition, the results of quantum chemical calculations for the O–CS_2 system will be presented.

In order to account for nonthermal flame propagation, Voronkov and Semenov [3] included reaction (V) and some other reactions into the hypothetical reaction scheme of CS_2 combustion. It was specified that this scheme is only one of the possible schemes and is presented only for the sake of definiteness. In the derivation of the expression for the flame velocity, reaction (V) was omitted. In the works in which this reaction was considered as a possible step of the carbon disulfide combustion scheme, its role in chain propagation was not analyzed. Some mechanisms (see, e.g., [11–13]) do not include this reaction at all. The critical CS_2 self-ignition conditions are not considered in these works. However, the fact that carbon disulfide is self-ignitable means that linear-law chain branching plays a significant role in its combustion. As a consequence, the reaction schemes that disregard reaction (V) cannot explain the observed self-ignition of CS_2, because, as was mentioned above, only this reaction yields atomic sulfur, the species capable of affording linear-law chain branching. Of course, not all of the resulting S atoms become involved in reaction (III). Under second-limit conditions, part of them enter into the termolecular chain termination reaction

$$S + O_2 + M = SO_3 + M. \qquad (VII)$$

A similar role in the process is played by the reaction

$$SO^{\bullet} + O_2 + M = SO_3 + M. \qquad (VIII)$$

Therefore, the effective chain branching rate is equal to the rate of reaction (V) multiplied by the fractions of S atoms and $SO^{\bullet}$ radicals that are involved in the chain propagation reactions (III) and (IV) (not (VII) and (VIII)).

It is obvious from the above that reaction (V) will supply sulfur atoms at a rate sufficient for self-ignition only if it competes efficiently with the loss of O atoms and ensures a rate of reaction (III) such that chain branching dominates over chain termination. The second self-ignition limit is known to be determined by the equality of the rates of bimolecular chain branching and termolecular chain termination (see, e.g., [5]). Therefore, by equating the chain branching and termination rates and using experimental self-ignition limit data, it is possible to determine the lower bound of the rate constant of reaction (V) (direct replacement of a sulfur atom in CS_2). Knowing this rate constant, it is possible to determine the upper bound of the activation energy. Agreement between the rate constant and activation energy data thus obtained and the corresponding literature data obtained by radically different methods would be evidence that reaction (V) plays the determining role in chain branching in carbon disulfide combustion.

Since the reaction limiting the chain branching rate involves atomic oxygen, the competing chain termination reaction must also involve this species. This termolecular termination reaction is

$$O + O_2 + M = O_3 + M. \qquad \text{(IX)}$$

Here, M is the third particle, which removes the recombination energy.

Ozone reacts readily with atomic oxygen, with the activation energy not exceeding 4 kcal/mol [13]:

$$O + O_3 = 2O_2. \qquad \text{(X)}$$

As a consequence, reaction (IX) is followed by additional partial removal of O atoms via reaction (X). In the second-limit critical self-ignition condition presented below, this fact is accounted for by a stoichiometric chain termination coefficient of 2. In view of what we said about the competing chain branching and termination reactions, we obtain the following relationship for the second self-ignition limit:

$$2k_5[CS_2]\beta = 2k_8[O_2][M]. \qquad (1)$$

Here, k_5 and k_8 are the rate constants of reactions (V) and (IX), $[O_2]$ and $[CS_2]$ are the O_2 and CS_2 concentrations, and [M] is the total concentration of the mixture at the second self-ignition limit. The coefficient 2 before k_8 accounts for the fact that chain branching increases the number of reactive intermediates by a factor of 2. The multiplier β stands for the product of the fractions of S atoms and $SO^\bullet$ radicals involved in reactions (III) and (IV), respectively.

Equation (1) enables one to calculate, from the second CS_2 self-ignition limit data presented in Fig. 1 and the k_8 value known from the literature, the product $k_5\beta$, which is the lower bound of the rate constant k_5, and then the upper bound of the activation energy of the direct substitution of an S atom in CS_2.

It is clear from Fig. 1 that the second-limit temperature range is very narrow. This is due to the instability of ozone, because of which the effective rate constant k_8 decreases greatly as the temperature rises. Therefore, k_5 can be determined only at moderate temperatures.

The O_2-to-CS_2 concentration ratio in this series of experiments was 700. According to Fig. 1, the mixture concentration at the second limit and $T = 473$ K is 5.18×10^{-6} mol/cm^3 (152 Torr). According to reference data recommended in [13], the rate constant of reaction (VIII) at this temperature is 5.6×10^{13} cm^6 mol^{-2} s^{-1}. By substituting these values into Eq. (1), we obtain a value of 2×10^{11} cm^3 mol^{-1} s^{-1} for the upper bound of k_5 at the given temperature. From this value and the fact that the preexponential factor is only slightly smaller than the number of binary collisions, we derive that the experimental upper bound of the energy barrier of reaction (V) is close to 6 kcal/mol.

Activated Complex of Reaction (V)

$$O(^3P) + CS_2 = OCS + S(^3P) \qquad \text{(V)}$$

The quantum chemical analysis of this reaction (direct replacement of a sulfur atom) was carried out by DFT calculations (B3LYP functional, 6-311G* basis set) using the Gaussian 98 program. The zero-point energy was taken into account. The transition state structures and the Gibbs energy diagram for the O + CS_2 system are presented in Fig. 2.

It was found that the planar triplet complex OCS_2, in which the bond lengths are O–C 1.188 Å and C–S 1.780 Å and the SCS angle is 95.1°, forms with an activation energy of 6.2 kcal/mol. The transition state TS1 is early (reactantlike), and, accordingly, the triplet complex forms with a large energy gain of 52.4 kcal/mol. The decomposition of this complex with the abstraction of an $S(^3P)$ atom is characterized by a low activation energy of 5.5 kcal/mol and an energy gain of 1.0 kcal/mol. The transition state TS2 of this reaction is also planar (bond lengths: O–C 1.163 Å, C–S^1 2.282 Å, C–S^2 1.642 Å; bond angles: S–C–S 118°, S^1–C–O 153°).

The lowest energy in the system is observed for the singlet adduct OCS_2 (see the structure at the bottom of Fig. 2), whose bond lengths are O=C 1.180 Å, C–S 1.770 Å, and S–S 2.220 Å. This adduct forms with an energy gain of 72.9 kcal/mol. The energy of its structural isomer SC(OS), which has bond lengths of S=C 1.590 Å, C–O 1.298 Å, C–S 1.792 Å, and S–O 1.857 Å, is 11.5 kcal/mol higher. Because the term of the singlet adduct OCS_2 correlates with the high-energy, excited, singlet term of the oxygen atom, this adduct, which is stable against decomposition into $S(^3P)$ + OCS, can result only from a nonadiabatic transition. Analysis has demonstrated that the related intersection of the potential energy surfaces of the singlet and triplet products takes place in the vicinity of the OCS_2 energy minimum on the triplet state surface. Therefore, taking into account that the transition state of the formation of the triplet product is 53.1 kcal/mol higher in energy than the transition state of its decomposition, we can infer

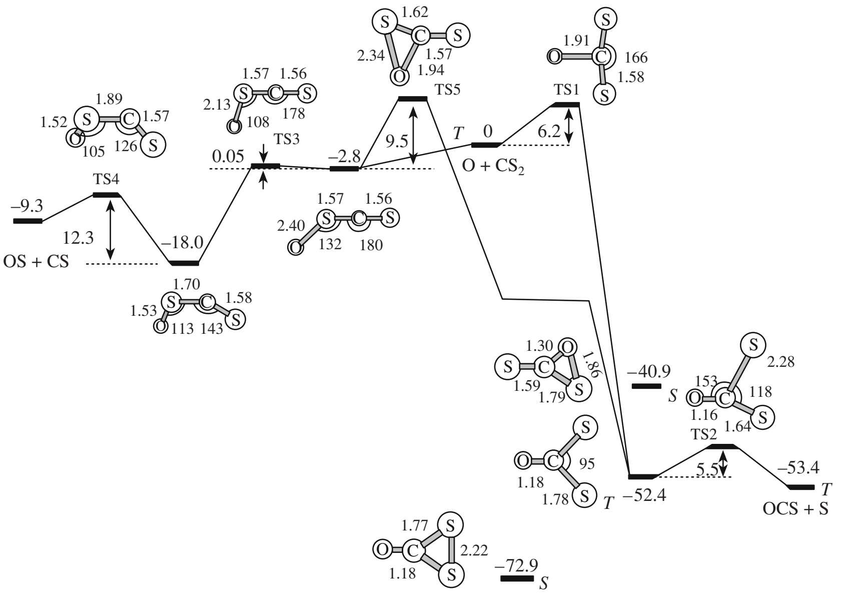

Fig. 2. Gibbs energy diagram for the interaction between the O atom and the CS_2 molecule. The transition state and product structures are shown. Bond lengths are in Å; angles, in deg; relative energies, in kcal/mol.

that this channel of the reaction between O and CS_2 results in the replacement of a sulfur atom.

The interaction between an oxygen atom and an S atom of the CS_2 molecule yields a weakly bonded adduct with an O–S bond length of 2.396 Å. This adduct transforms, with a low activation energy of 0.05 kcal/mol, into a complex between an SO and a CS molecule in which the C–S bond length is 1.696 Å. The energy gain in this transformation is 15.2 kcal/mol. The main change occurring in the transition state of this process (TS3) is the change in the O–S–C angle. As this takes place, the linear structure of CS_2 remains almost undistorted. The decomposition of the complex between SO and CS requires a fairly high energy of 8.7 kcal/mol. The activation energy of this decomposition is even higher (12.3 kcal/mol). The transition state of this process (TS4) is nonplanar. The torsion angle O–S–C–S is 86.1°, and the S–C bond distance is 1.893 Å. The lengths of the S=O bond (1.518 Å) and the C=S bond (1.571 Å) differ only slightly from the bond length that we calculated for the respective molecules (1.510 and 1.538 Å). The corresponding experimental data are 1.481 and 1.535 Å.

Thus, the S atom abstraction channel of the reaction between the O atom and the CS_2 molecule mainly yields the metastable complex between SO and CS. It is likely that the SO molecule in this complex participates in chain propagation reactions, but with a lower efficiency than the free SO molecule. The reactivity of SO in its complex with CS can manifest itself as the intramolecular transformation of the O=S…C=S complex into the energetically much more favorable triplet product O=CS_2 followed by the elimination of an S atom. However, our calculations failed to locate the corresponding transition state. We identified only the transition state in the conversion of the adduct O…SCS into the O atom addition product O=CS_2 (TS5). This transition state is asymmetric and is similar in properties to TS1. The states TS5 and TS1 are energetically very similar. If the activation energy of the decomposition of the O=S…C=S complex (12.3 kcal/mol) is close to the activation energy of the conversion of this complex into O=CS_2, the second reaction channel will also yield an S atom, but the activation energy of this process will be higher than that of direct replacement.

The above results of quantum chemical calculations are in agreement with the analysis of experimental second self-ignition limit data. The calculated activation energy of reaction (V) differs only slightly from the values reported in [16, 17]. Our lower bound of is in agreement with the value of this rate constant known from [16] for the temperature considered (4.5×10^{11} $cm^3 \times mol^{-1} s^{-1}$). It is also in agreement with the rate constant reported in [22] for $T = 298$ K under the assumption that the effective activation energy is similar to that reported in [16]. Equally good agreement with our data will be observed if one uses the values reported in [19, 23].

Thus, reaction (V) ensures the regeneration of sulfur atoms, which are branching chain carriers, competing successfully with the oxygen atom disappearance reaction.

In developed combustion, including flame propagation, a significant role is played by nonlinear-law chain branching. However, even in this combustion regime, the key role is played by the chain propagation reaction (V), which serves as the source of the sulfur atoms responsible for the multiplication of reactive intermediates.

The exponent in the expression for the rate constant reported in [12], which corresponds to the activation energy 1.4 kcal/mol, is also in agreement with our upper bound of the energy barrier.

Finally, note that nonlinear-law chain branching is of significance in developed combustion, including flame propagation. However, in this combustion regime and at higher temperatures, the key role is played by the chain propagation reaction (I): it generates sulfur atoms, which are necessary for the multiplication of reactive intermediates.

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