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# The Role of a Reaction of Direct Substitution for a Sulfur Atom in the $CS_2$ Molecule in the Combustion of Carbon Disulfide with Oxygen

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**Abstract**—In the combustion of carbon disulfide, the direct substitution reaction $O + CS_2 = OCS + S$ (I) was found to be the main source of atomic sulfur, which is responsible for the branching of reaction chains. As distinct from the reactions of intermediate products with each other, step (I), which is a first-order reaction with respect to the concentration of chain carriers, together with an act of multiplication of active species, is responsible for not only flame propagation but also critical self-ignition conditions.

It is well known that carbon disulfide is a highly inflammable compound. Its vapor self-ignites in air even at 100°C and at low pressures. The combustion of $CS_2$ is a chain reaction; that is, it is primarily due to the avalanche multiplication of active intermediate species (chain carriers). This reaction exhibits characteristic properties of branched-chain processes. Great inflammability is an indicator of the occurrence of a fast reaction of chain branching in the process mechanism. The combustion of carbon disulfide is known in the theory of chemical kinetics mainly because of the fact that the flame-propagation regime that does not require an increase in the temperature of a reaction mixture predicted by Zel'dovich and Frank-Kamenetskii [1] was supported experimentally using this reaction as an example [2]. This regime of “nonthermal” flame propagation is caused by the avalanche multiplication of active intermediate species as a result of their reactions with each other. The subsequent studies were devoted to the regularities of nonthermal flame propagation in the mixtures of $CS_2$ with air and oxygen and to the identification of active intermediate species—reaction chain carriers in the flame zone (for example, [3–10]). Azatyan *et al.* [10] obtained the propagation characteristics of a nonthermal carbon disulfide flame in air by the numerical solution of sets of equations. Because the use of a great number of calculated parameters was responsible for unavoidable uncertainty in quantitative results, it was beyond the scope of the cited work [10] to achieve an agreement between the calculated and measured values of self-ignition limits and flame propagation rates.

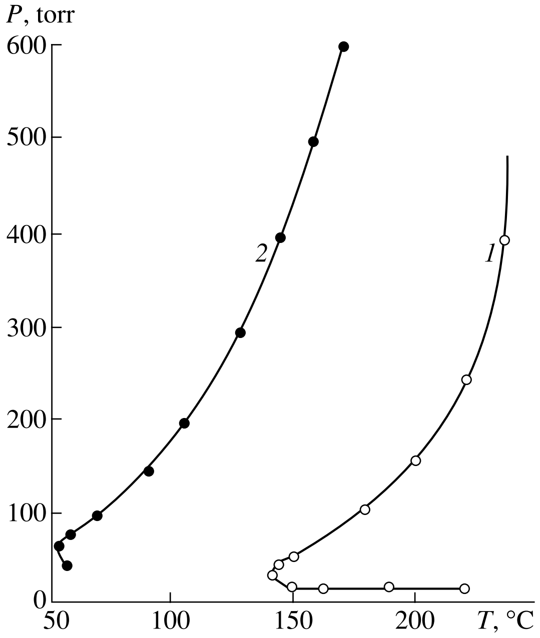
In the region of self-ignition limits, the process mechanism is incomparably simpler, and a much smaller number of parameters are required for the calculation. Moreover, equations for self-ignition limits are much simpler. Nevertheless, the calculated values of self-ignition limits [10] are dramatically different from the experimentally measured values [2]; this is mainly due to inaccuracies in the rate constants known by the time the calculations were performed.

By now, the rate constants of many main reactions of the processes have been determined by various techniques to reliable accuracies. At the same time, the detailed mechanism of carbon disulfide oxidation remains unknown. Therefore, many regularities of the combustion, including dramatic changes in the main kinetic characteristics of the process and in the color of a flame on varying the ratio between the initial concentrations of components near a stoichiometric composition, still remain unexplained.

This work is devoted to studying the role of the direct reaction of sulfur atom displacement from the $CS_2$ molecule by atomic oxygen:

$$O + CS_2 = COS + S. \qquad \text{(I)}$$

Note that this reaction, along with other reactions, was included in the hypothetical reaction scheme of $CS_2$ combustion [3]. However, in this case, it was specified that the proposed scheme is only one of the conceivable schemes, which was only given for clarity. The rate constant of reaction (I) does not appear in an expression for the rate of flame propagation, which was derived on a number of assumptions. This reaction is a conceivable step of carbon disulfide combustion in reaction schemes given in other publications. However, the role of reaction (I) in the development of reaction chains was not analyzed, and this reaction was completely absent from the mechanisms proposed, for example, in [11–13]. The critical conditions of $CS_2$ self-ignition were not considered in the above publications. However, as discussed below, reaction schemes that do not take into account reaction (I) cannot explain



Limiting pressures of (*1*) self-ignition and (*2*) nonthermal flame propagation in a mixture of 0.03% $CS_2$ in air according to published data [2].

the observed self-ignition of $CS_2$ at moderate temperatures and pressures.

Here, the role of reaction (I) in the combustion of carbon disulfide is evaluated with consideration for data on the inflammability of the vapor of this compound in air and based on a comparison of the rate of this process with the rates of the main steps of the combustion. For this purpose, the concentrations of reactants at the second self-ignition limit, which were given in [2, 3] (figure), and the known reaction rate constants of the main steps of chain propagation and termination were used. The critical conditions of self-ignition were chosen because these conditions depend only on a small number of steps that play an important role in the development of spontaneous combustion. This provides unambiguous conclusions. Moreover, the concentrations appearing in the equation for ignition limits relate to only parent reactants and the initial moment of self-ignition; that is, they are the initial concentrations of the parent reactants. Evidently, the measurement accuracy of these concentrations is much greater than the measurement accuracy of the concentrations of active intermediate products and the characteristics of flame propagation. It was preferable to choose the second self-ignition limit because both chain branching and chain termination (competition between them is responsible for a critical condition of self-ignition) occurred in the gas phase. Because of this, the knowledge of the rate constants of heterogeneous reactions is not required. These rate constants depend on the material and state of a surface, except for specially produced conditions under which diffusion becomes a rate-limiting process [14]. These conditions were not produced in the studies reported [2, 3].

Because a self-ignition regime and its critical conditions were chosen in this study, attention must be given to the following: It is well known that self-ignition is a reduction regime that occurs in a reaction mixture that has the same initial temperature over the entire reaction volume. In this regime, combustion begins spontaneously without local initiation [3, 15]. A prerequisite for the appearance and development of chain combustion is an excess of the rate of chain branching over the rate of chain termination [3]. Under critical conditions of self-ignition, in fact, there are no reactions between active species, which result in the multiplication of these species. Therefore, if chain combustion begins by self-ignition, an active intermediate species, reacting with only the molecule of a parent reactant, is responsible for chain branching. Thus, the reaction rate of chain branching in self-ignition is proportional to the first power of the concentration of active intermediate species (chain carriers). This type of the kinetics of branching is sometimes referred to as “linear branching,” implying that the rate of branching is a linear function of the concentration of chain carriers. The chemical nature of an act of spontaneous generation of reaction chains, that is, a reaction that occurs with the participation of only initial molecular reactants without artificial stimulation, does not define the limit value because the rate of this reaction is extremely low.

The following active intermediate species were detected in the flames of carbon disulfide mixtures with oxygen using EPR and optical spectroscopy: atomic oxygen, SO radicals, and stable intermediate products (COS, CO, CS, and $S_2$) [4–8]. The dependence of the concentrations of intermediate products on the initial composition of the mixture was found [6, 7]. The rate constants of almost all the main steps of the process are also known [16–22]. These data were used in the comparison between the rates of linear steps given below and in the determination of the role of these steps in competition between chain branching and termination.

The reaction

$$O + CS_2 = SO + CS \tag{II}$$

is not an act of the multiplication of chain carriers because, among its products, only the SO radical in the given mixture can propagate reaction chains. Under the specified conditions, the CS molecule is not an active species, and it cannot participate in the development of reaction chains. Indeed, at the ignition limit, CS can react only with $O_2$:

$$CS + O_2 = COS + O. \tag{III}$$

However, the activation energy of this reaction is greater than 15 kcal/mol, and its rate constant is lower than $2 \times 10^6$ cm$^3$ mol$^{-1}$ s$^{-1}$ [18]. It is clear, taking into account the rate of $CS_2$ consumption in ignition under the specified conditions (figure), that reaction (III) has not managed to participate in chain ignition and combustion at least at temperatures lower than 500 K because of the small rate constant. This was supported by experimental results, which demonstrated that CS was deposited on the walls. Because the rate of reaction (III) is insignificant, only reaction (II) is a step of chain propagation, in which the O atom is replaced by another active intermediate species, SO, which is also a biradical. At the same time, the self-ignition of carbon disulfide, especially, at low temperatures and pressures, is indicative of the occurrence of branching, which is linear with respect to the concentration of chain carriers. The following reaction results in the formation of two active intermediate species:

$$S + O_2 = SO + O. \qquad (IV)$$

The products of reaction (IV) can initiate new branches of the reaction chain via reaction (II) and the parallel step

$$SO + O_2 = SO_2 + O. \qquad (V)$$

Thus, at step (IV), atomic sulfur multiplies active species. The published rate constants of reaction (IV) at the center of the temperature range under consideration (483 K) are very great and equal to $1.4 \times 10^{12}$ [18] and $3.3 \times 10^{11}$ cm$^3$ mol$^{-1}$ s$^{-1}$ [20]. However, this reaction can result in linear chain branching only in the case when the rate of the reaction that supplies sulfur atoms for the chain process is not only great but also linearly depends on the concentration of active species. It is evident that the reaction of S atom formation

$$SO + SO = SO_2 + S, \qquad (VI)$$

which was given in a number of published reaction schemes, cannot play a considerable role under critical conditions of self-ignition, even if its rate constant is great, because this is the interaction of active species with each other, that is, nonlinear with respect to the concentration. For the same reason, the following reaction cannot play a considerable role under critical conditions of self-ignition:

$$O + CS = CO + S.$$

As distinct from these reactions, step (I) of the direct displacement of a sulfur atom from $CS_2$ is linear with respect to the concentration of active species—atomic oxygen.

The capability of $CS_2$ and air mixtures for self-ignition even at low temperatures and concentrations (for example, see the figure) suggests that the rate of reaction (I) is as great as the rates of the other main steps of the chain process. This reaction can serve as a supplier of sulfur atoms at a rate required for self-ignition only when it not only efficiently competes with the decay of O atoms but also provides the rate of reaction (III) at which chain branching predominates over chain termination. It is well known (see, for example, [3]) that chain termination, which is responsible for the second limit, should be limited by a termolecular reaction. Thus, if the rate of reaction (I) is greater than the rate of the termolecular chain termination

$$O + O_2 + M = O_3 + M \qquad (VII)$$

at the second limit of self-ignition, reaction (I) is one of the most important steps in the mechanism of $CS_2$ combustion. Here, M is the third particle that removes energy released in the recombination. The above condition corresponds to the following relation:

$$k_7[O_2][M] < k_1[CS_2], \qquad (1)$$

where $k_7$ and $k_1$ are the rate constants of reactions (VII) and (I), respectively; [M], $[O_2]$, and $[CS_2]$ are the total concentration of the mixture and the concentrations of $O_2$ and $CS_2$ at the second limit of self-ignition, respectively. For example, at the center of the temperature range shown in the figure (480 K), the rate constant of reaction (VII) is equal to $5.6 \times 10^{13}$ cm$^6$ mol$^{-2}$ s$^{-1}$ [17]. At the specified temperature, the pressure at the second limit is equal to 28 kPa (210 torr), which corresponds to the concentration of the mixture equal to $6.9 \times 10^{-6}$ mol/cm$^3$. Taking into account the above value of $k_7$ and the mole fractions of $O_2$ and $CS_2$ equal to 0.21 and $3 \times 10^{-4}$, respectively, using expression (1), we obtain $k_1 > 2.7 \times 10^{11}$ cm$^3$ mol$^{-1}$ s$^{-1}$. From this great rate constant and a maximally possible preexponential factor for bimolecular reactions, it follows that the energy barrier of reaction (I) of the direct displacement of a sulfur atom is no greater than 13 kJ/mol.

The value of $k_1$ obtained is consistent with the published value of this constant equal to $5.1 \times 10^{11}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at the specified temperature [16] and with the reported value of $k_1$ for 298 K [22], if the effective activation energy was taken close to that published in [16]. The use of the values of $k_7$ proposed in [19, 23] also resulted in good agreement with our results.

Thus, reaction (I), being the main source of atomic sulfur, which is responsible for reaction chain branching, efficiently competes with the reaction of atomic oxygen decay. Because the rate of this reaction linearly depends on the concentration of chain carriers, it, together with the acts of chain branching and termination, determines the limit of ignition.

Note that, along with the above reactions, the following reactions should also be taken into consideration for the quantitative description of the second limit of $CS_2$ ignition:

$$SO + O_2 + M = SO_3 + M,$$

$$S + O_2 + M = SO_3 + M.$$

However, the rate constants of these reactions were determined to a lower accuracy.

The role of nonlinear chain branching becomes important in developed combustion and, in particular, flame propagation. However, reaction (I) of chain propagation also plays the role of the main source of atomic sulfur, which is required for the multiplication of active intermediate species, in this combustion regime. An analysis of competition between reactions (I) and (VII) with consideration for the rate constants demonstrated that reaction (I) of the direct displacement of a sulfur atom together with reaction (IV) of the multiplication of chain carriers in developed combustion are the most important steps, which are also responsible for chain branching at temperatures that are much greater than those considered in this work.

The activation energy equal to 5.9 kJ/mol, which is also consistent with the above upper limit of the energy barrier, corresponds to the exponent $n$ in the expression reported by Singleton and Cvetanovic [16] for the rate constant. However, the value of 5.9 kJ/mol should be considered only as an effective activation energy because the rate constant was presented in Arrhenius form [16]. Indeed, the contribution of the temperature dependence of a preexponential factor, which contains the partition functions of the reactants and the activated complex, is particularly noticeable in such reactions with the rate constants weakly dependent on temperature.

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## REFERENCES

1. Zel'dovich, Ya.B. and Frank-Kamenetskii, D.A., *Zh. Fiz. Khim.*, 1938, vol. 12, no. 1, p. 100; *Dokl. Akad. Nauk SSSR*, 1938, vol. 19, p. 693.
2. Voronkov, V.G. and Semenov, N.N., *Zh. Fiz. Khim.*, 1939, vol. 13, no. 11, p. 1695.
3. Semenov, N.N., *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* (On Some Problems of Chemical Kinetics and Reactivity), Moscow: Akad. Nauk SSSR, 1958.
4. Azatyan, V.V., Sarkisyan, E.Ya., and Nalbandyan, A.B., *Dokl. Akad. Nauk SSSR*, 1964, vol. 158, no. 1, p. 179.
5. Azatyan, V.V., Gershenson, Yu.M., Sarkisyan, E.N., and Nalbandyan, A.B., *Proc. 11th Symp. (International) on Combustion*, Poitier, 1968, p. 801.
6. Sarkisyan, E.N., Azatyan, V.V., and Nalbandyan, A.B., *Dokl. Akad. Nauk SSSR*, 1968, vol. 178, no. 2, p. 389.
7. Sarkisyan, E.N., Azatyan, V.V., and Nalbandyan, A.B., *Dokl. Akad. Nauk SSSR*, 1972, vol. 203, no. 4, p. 888.
8. Kondrat'ev, V.N., *Kinet. Katal.*, 1972, vol. 13, no. 6, p. 1367.
9. Davis, D.D., Thrush, B.A., and Pilling, M., *Int. J. Chem. Kinet.*, 1972, vol. 4, no. 2, p. 367.
10. Azatyan, V.V., Novozhilov, B.V., Posvyanskii, V.S., and Semenov, N.N., *Kinet. Katal.*, 1976, vol. 16, no. 6, p. 1386.
11. Wood, W.P. and Heicklen, J., *J. Phys. Chem.*, 1971, vol. 75, no. 7, p. 861.
12. Kondrat'ev, V.N. and Nikitin, E.E., *Kinetika i mekhanizm gazofaznykh reaktsii* (Kinetics and Mechanism of Gas-Phase Reactions), Moscow: Nauka, 1973.
13. Gordon, G.B., *Tsepnye reaktsii* (Chain Reactions), Semenov, N.N., Ed., Moscow: Nauka, 1987, p. 528.
14. Denisov, E.T. and Azatyan, V.V., *Inhibition of Chain Reactions*, London: Gordon and Breach, 2000.
15. Combustion, in *Khimicheskaya entsiklopediya* (Chemical Encyclopedia), Moscow: Sovetskaya Entsiklopediya, 1988, vol. 1, p. 828.
16. Singleton, D.L. and Cvetanovic, R.J., *J. Phys. Chem. Ref. Data*, 1988, vol. 17, p. 1377.
17. Atkinson, R.F., Baulch, D.L., Cox, R.A., Hampson, M.J., Kerr, J.A., Rossy, M.J., and Troe, J., *J. Phys. Chem. Ref. Data*, 1997, vol. 26, p. 1329.
18. Chang, K., Kalvert, J.G., and Rotteheim, J.W., *Int. J. Chem. Kinet.*, 1975, vol. 7, p. 161.
19. Martine, R.J. and Herron, J.T., *Int. J. Chem. Kinet.*, 1983, vol. 15, p. 1127.
20. Seheted, J., Neilson, O.J., Egsgard, H., *et al.*, *J. Geophys. Res.*, 1998, vol. 103, p. 3545.
21. Tsuchiya, K., Kamiya, K., and Matsui, H., *Int. J. Chem. Kinet.*, 1997, vol. 29, p. 57.
22. Cooper, W.F. and Hershberger, J.F., *J. Phys. Chem.*, 1992, vol. 96, p. 5405.
23. Kondrat'ev, V.N., *Konstanty skorosti gazofaznykh reaktsii* (Rate Constants of Gas-Phase Reactions), Moscow: Nauka, 1970.