

EXTENT OF CARBON DISULPHIDE PHOTODISSOCIATION AND THE KINETIC LENGTH OF ITS OXIDATION CHAIN ESTIMATED BY MEANS OF A CS₂/O₂ LASER

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Summary

The extent of carbon disulphide photodissociation ϵ and the mean length of its oxidation chain were measured by means of a CS₂/O₂ laser. The kinetic chain length near the ignition limit appeared to be very low ($\nu = 1$ to 3) for all pressures and mixture compositions studied. These results made clear (seemingly for the first time) the high probability of branching in carbon disulphide oxidation (*i.e.* that oxidation occurred by the mechanism of virtually complete branching).

The simple procedure of determination of the extent of photodissociation ϵ can be applied to other laser systems as well.

Introduction

Chain-branching oxidation of carbon disulphide displays certain specific features. Of great importance are the time anomalies in the development of spontaneous chain ignition, namely the large ignition delay (several tens of seconds and more) followed by fast acceleration of the process (faster than a millisecond) [1]. In normal chain-branching reactions the ignition delay is comparable with the time of reaction [2]. Thus, branching in the given reaction is of a specific nature.

On the other hand, carbon disulphide oxidation is widely used in pulsed chemical CO lasers [3, 4]. At low pressures ($p_{\text{CS}_2} < 1$ Torr) these lasers very effectively convert the chemical energy into coherent radiation on the vibrational transitions of CO (6% chemical efficiency), but at high pressures (or in mixtures diluted with inert gases) the laser energy rapidly drops obeying the termolecular kinetic law [5]. This can be accounted for neither by vibrational relaxation of CO molecules on the gas added (it would have an effect at pressures at least by two orders of magnitude higher than those used), nor by any chemical termolecular process of the chain carrying

species decay. A suggestion has been made in a previous paper [5] that a sufficiently long kinetic chain ($\nu = 10$ to 30) developing in 10 to $20 \mu\text{s}$ may be realized under laser conditions. In this case the observed quenching of laser emission by pressure would be accounted by a chemical termolecular reaction of type $\text{S} + \text{CS}_2 \xrightarrow{\text{M}} \text{CS}_3$.

The relation:

$$\eta = \epsilon(\nu + 1) \quad (1)$$

is obviously valid for a light-induced chain reaction. Here ϵ is the extent of photodissociation, η is the extent of CS_2 photodecomposition (both in photodissociation and in a chemical reaction), ν is the kinetic length of the chain.

Thus, for carbon disulphide oxidation ν can be estimated from known η and ϵ . Knowledge of ν and ϵ is important for understanding both the CS_2/O_2 laser operation and the reaction mechanism in general.

The present paper deals with determination of η and ϵ , and of the relevant kinetic chain length ν under laser conditions.

Principle of method

Determination of the CS_2 photodecomposition extent by spectroscopy in vacuum u.v. [6] or by gas analysis (for instance, by mass spectroscopy) requires the use of particular techniques and is very laborious. No less complicated is the technique proposed by Wright [7] and based on photometry of SO_2 formed by combustion in oxygen of the pulsed $\text{CS}_2 + \text{CO}_2$ photolysis products deposited on the reaction vessel wall*.

Our results obtained in investigating chemical CS_2/O_2 lasers [4, 5] permitted proposing a simple method for estimation of the extent of CS_2 photodissociation and of the quantum yield of CS_2 decomposition in the branched chain reaction $\text{CS}_2 + \text{O}_2$.

It was found that within a certain range of experimental conditions lasing in the CS_2/O_2 laser occurs upon repetitive initiation as well. As distinct from such phenomena observed for the photodissociation [9], chemical [10], and other lasers displaying a monotonic decrease in emission energy and power from flash to flash, in the given case the lasing may become stronger with higher flash numbers and even, under properly chosen conditions, it may start after a fixed number of flashes. This effect is seen in Fig. 1 for an initial pressure of mixture such that the partial CS_2 pressure p is higher than that corresponding to the maximum laser power, p_{opt} (Fig. 2). On repetitive u.v. initiation of the mixture the power (the energy) of

*It is just for this reason that many authors [8] direct use ϵ values obtained in refs. [6] or [7]. However, the strong dependence of u.v. emission ($180 < \lambda < 200$) absorbed by carbon disulphide on the quality of optical material commonly used for the reactor and the flash lamps decreases the reliability of such estimates.

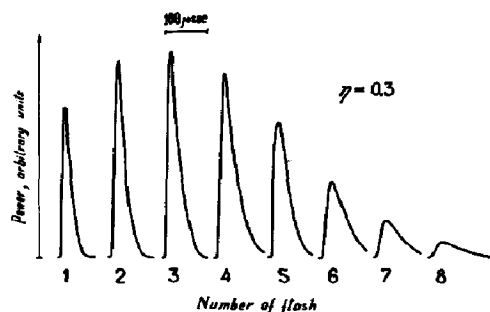


Fig. 1. Laser impulses at a repetitive initiation ($W_k = 1.2$ kJ; $\text{CS}_2/\text{O}_2/\text{He} = 1 : 10 : 22$).

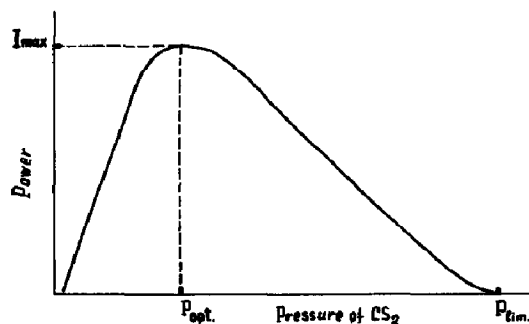


Fig. 2. Typical function of the laser power on CS_2 pressure.

emission first increases up to a certain maximum close to I_{\max} (I for $p = p_{\text{opt}}$), and then drops to zero. The higher power of initiation results in a lower number of flashes accompanied by lasing. If p is higher than p_{thresh} above which lasing terminates, the laser action will commence by one of the successive flashes. At pressures $p < p_{\text{opt}}$ the power of emission drops monotonically.

Such a laser emission's behaviour is an unambiguous result of u.v.-induced CS_2 consumption [4], as distinct from all other lasers for which the decrease in emission upon repetitive shots is due to quenching of active atoms (molecules) on the products of a photochemical reaction [9].

The above effect was used in estimating the concentration of carbon disulphide in the mixture to the start of initiation. Knowing this concentration it was possible to obtain the extent of u.v.-induced CS_2 consumption in a chemical CO laser and the mean length of the disulphide oxidation chain under these conditions.

Experimental

The apparatus used has been described in detail earlier [4, 5]. An optical quartz cell (transparent up to 200 nm) was placed inside an optical cavity. Initiation was realized by two alternating xenon flash lamps (xenon pressure about 20 Torr) made of the same material as that of the cell. The flash lamps and cell were surrounded by a cylindrical reflector of aluminium foil. The pulse length was about 8 μs . The laser emission was registered by means of a Ge: Au (77 K) photoresistance.

Carbon disulphide was purified of its decomposition products by distillation over CaCl_2 and subsequent treatment with potassium permanganate, mercury, mercury sulphate, and redistillation over CaCl_2 . The oxygen and helium used were commercial.

The mixture was prepared either by premixing in a special vessel, or by sequential inlet of components directly to the reactor. This had no influence on the laser characteristics.

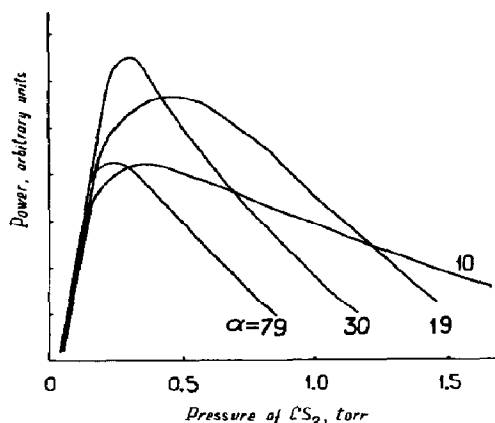


Fig. 3. Laser power vs. CS₂ pressure for various values of α .

Results

Estimation of ϵ

Carbon disulphide oxidation is a chain reaction and, consequently, the extent of CS₂ photoconsumption exceeds that of photodissociation ϵ . In order to prevent chemical consumption, carbon disulphide had to be u.v.-irradiated in the absence of oxygen. The following procedure was used accordingly.

At an initial pressure p_0 carbon disulphide in a mixture with helium ($I([\text{He}]/[\text{CS}_2] \equiv x)$) was u.v.-flashed k times. After that oxygen was let in to a pressure corresponding to the initial value $\alpha \equiv [\text{O}_2]/[\text{CS}_2]$, and upon the time needed for static intermixing (in 1 to 5 min) the lasing was realized in the $(k + 1)$ th flash. As stated above, laser emission intensity I_{k+1} is a function of partial CS₂ pressure retained after a k number of preceding pulses, p_k , *i.e.*

$$I_{k+1} = f(p_k)$$

The $f(p_k)$ function was obtained as follows. Carbon disulphide premixed with oxygen and helium was let into the cell up to a certain pressure and was excited by a single u.v. flash. Then, the dependence of the lasing power on partial CS₂ pressure $I_1(p)$ was calibrated for constant mixture parameters α , x and a constant initiation energy W (of the type in Fig. 2).

Strictly speaking repetitive u.v. irradiation brings about a change in the mixture composition, *i.e.* in the parameters α and x . But it was found that at CS₂ pressures lower than the optimum one $I_1(p)$ was virtually independent of α (Fig. 3) and of x [5]. Consequently, the dependence $I_1(p; \alpha = \text{constant}, x = \text{constant})^*$ can be used in calibrating the above range of CS₂ pressures.

*The range of initial CS₂ pressures can be widened by calibrating over the dependence of emission power on CS₂ pressure at a fixed O₂ pressure.

In our experiments the mixture is optically thin and thus, assuming that the absorption spectrum and quantum yield of CS₂ photodissociation ϵ will also be pressure independent. Then, the partial CS₂ pressure after producing (k) pulses, p_k , will be:

$$p_k = p_0(1 - \epsilon)^k \quad (2)$$

or

$$\log p_k = \log p_0 + k \log (1 - \epsilon) \quad (3)$$

Partial CS₂ pressures after producing k pulses ($k = 1, 2, 3, \dots$) were estimated from the intensity of laser emission in the ($k + 1$) pulse (I_{k+1}), making use of the above-mentioned calibration curve. The experimental data processing by eqn. (2) gave ϵ values with a 20% scatter. For instance, in the range of CS₂ pressures $p_0 = 0.4$ Torr at an initiation energy $W = 1.2$ kJ, ϵ appeared to be 0.1 ± 0.02 .

Estimation of η

The extent of CS₂ consumption in its photooxidation was estimated from variations in laser emission intensity upon repetitive initiation.

The mixture was diluted with helium to prevent its thermal entrance into the ignition peninsula as a result of u.v. absorption. Otherwise carbon disulphide would be completely consumed in the first flash. The carbon disulphide consumption by a series of successive flashes was estimated from the maximum laser's power in the k th flash, I_k .

Generally speaking, the kinetic length of the chain ν , and consequently the extent of CS₂ consumption η , must depend on CS₂ pressure. However, the experimental curves linearize in coordinates $\log p_k$ vs. k , and this indicates the constancy of η . Figures 4a and 5a are examples of $\log p_k$ as a function of the flash number k . Figure 4a corresponds to an initial CS₂ pressure higher than the optimum one ($p > p_{opt}$) (Fig. 5a, to $p_0 < p_{opt}$).

Points (I_{k+1}, p_k) in Figs. 4b and 5b are representative of p_k calculated by dependence (2) for relevant values $\eta = 0.28$ and $\eta = 0.32$. As seen from Figs. 4 and 5 the law of variations in CS₂ pressure with flash numbers (2) is quite consistent with the experimental results. For $p < p_{opt}$ this agreement takes place down to the lasing threshold on the side of low partial CS₂ pressures.

The results of experiments with repetitive flashes in four mixtures of CS₂/O₂/He = 1:10:22, 1:10:55, 1:10:121, 1:10:253 at an initiation energy $W_k = W = 1.2$ kJ seem to show that the extent of CS₂ consumption per flash does not depend on mixture dilution with inert gas and appears to be 0.3 ± 0.04 .

Discussion

Experiments have shown that over a rather wide range of CS₂ pressures and at various dilutions of the CS₂-O₂ mixture with helium ($x \equiv [\text{He}]/[\text{CS}_2]$)

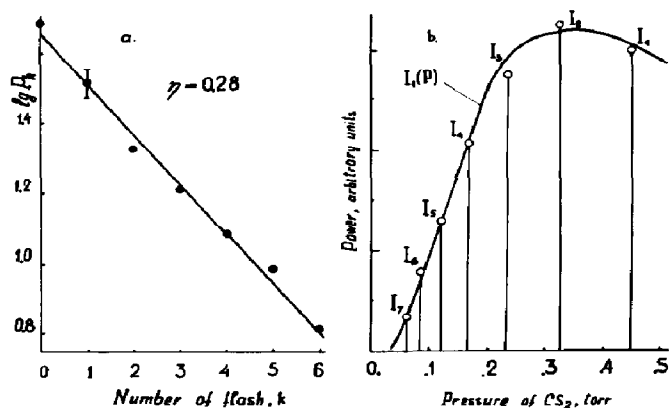


Fig. 4. The case $p_0 > p_{opt}$ for the estimation of η values. (a) $\log p_k$ vs. flash number k ; (b) laser power vs. CS_2 pressure; $I_1(P)$ (solid curve); laser power in the flash number " $k+1$ "— $I_{k+1}(P_k)$ for estimated $\eta = 0.28$.

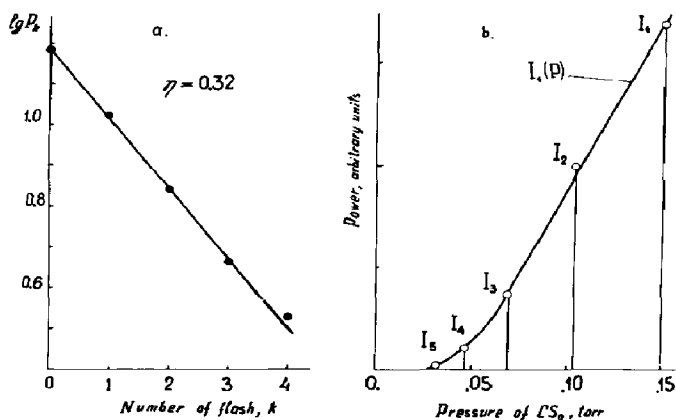


Fig. 5. The case $p_0 < p_{opt}$ for the estimation of η values. (a) $\log p_k$ vs. flash number k ; (b) laser power vs. CS_2 pressure; $I_1(P)$ (solid curve); laser power in the flash number " $k+1$ "— $I_{k+1}(P_k)$ for estimated $\eta = 0.32$.

= 22 to 253) the kinetic length of a chain is:

$$\nu = \frac{\eta}{\epsilon} - 1 = \frac{0.30 \pm 0.04}{0.10 \pm 0.02} - 1 = 1 \text{ to } 3^*$$

It will be noted that the calculated value represents the overall length of the chain, involving all steps of CS_2 oxidation. It will be seen that the kinetic scheme of fast chemical reactions that can contribute to the chain during the 10 - 20 μs of generation proposed in ref. [5]:

*The very low chain length values account for its independence of CS_2 pressure and mixture dilution with inert gas.



yields $\nu_{\text{fast}} = 1$. With long times of reaction contribution can be given by reactions involving low-active radicals CS and SO. What is more, such reactions are bound to occur, since the scheme of fast reactions (I) - (IV) does not involve a branching process, whereas the reaction $\text{CS}_2 + \text{O}_2$ is known to be chain branching. A reaction leading to fast chain branching



has been proposed [5] as an explanation to dependence of the CS_2/O_2 laser action on pressure.

The results obtained here ($\nu - \nu_{\text{fast}} = 0$ to 2) seem to show that processes of type (V) either do not contribute to oxidation, or their contribution is of a low efficiency, as the faster decay of active centres competes with (V).

In any case it appears that the kinetic length of the chain remains very low up to the chain ignition limit*. This fact can find an explanation only under the assumption of virtually complete branching of the CS_2 oxidation chain.

Indeed, the condition for branched chain ignition can be written as [11]:

$$\delta \cdot \nu = 1 \quad (4)$$

where δ is the probability of branching per one step of the chain. The results obtained seem to show that $\delta \sim 1$, *i.e.* that the branching inside the ignition peninsula occurs virtually at every step.

As stated above, one of the incentives for this research was the necessity of testing the assumption that photo-induced CS_2 oxidation represented a fast chain with $\nu = 10$ to 30. This assumption was put forward in order to explain the rapid (termolecular) pressure-induced drop of laser energy and power in a CS_2/O_2 laser. At pressures resulting in a drop of the emission power, no conceivable termolecular processes can compete with the bimolecular processes (I) - (III) yielding vibrationally excited CO^* molecules. A fast kinetic chain, for instance as a result of reactions $\text{O} + \text{CS}_2 \longrightarrow \text{OCS} + \text{S}$ (IIa) or (V), provided an explanation to this controversy.

However, the results obtained here show that even a slow chain of CS_2 oxidation is very short and the inconsistency of the limiting termolecular

* An increase in initiation energy by 30 - 40% results in complete consumption of carbon disulphide, as pulsed heating drives the mixture into the ignition peninsula.

termination step and of its calculated rate with the rates of bimolecular processes remains an unsolved problem.

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