ON THE CHARACTERIZATION
OF CO_2 LASER PHOTOSENSITIZED REACTIONS

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The study of the effect of some variable parameters of the *cw* CO_2 laser photosensitized reactions as concentration of inert gas and sensitizer, and laser output upon the temperature distribution inside the reactor is presented together with the application of two kinetic approaches to the laser photosensitized (SF_6) dehydrochlorination of 1,1,1-trichloroethane.

The laser powered homogeneous pyrolysis[1] occurs strictly in the gas phase without involvement of surface effects, which makes it useful for the estimation of heterogeneous stages taking place on the hot reactor surfaces in conventional pyrolyses. The reaction rate of the laser induced process can be estimated on the basis of the knowledge of the distribution of temperature in a reactor exposed to the laser radiation[2]. The temperature distribution is affected by several parameters[3]. Two models have been put forward to characterize the hot zone, *i.e.* a volume wherein the reaction occurs. The first model[2,4] presumes the reaction to occur within the limited space in a close proximity of the entrance reactor window, the second one[5] suggests that the reaction takes place throughout the entire reactor volume at the effective temperature calculated on the basis of the experimentally ascertained rate constant and the Arrhenius parameters (activation energy and frequency factor) of a standard chemical reaction.

In connection with our previous study of spatial temperature distribution in *cw* CO_2 laser photosensitized reactions[6] we wish in this communication to show the way in which is the temperature distribution influenced by some variable reaction parameters, and we want further to examine the applicability of the two aforementioned models of the hot zone to the dehydrochlorination of 1,1,1-trichloroethane.

EXPERIMENTAL

The experimental procedure of the measurement of the temperature distribution in a vertically positioned tube-like reactor (36 mm i.d., 100 mm long) irradiated with a *cw* CO_2 laser was reported elsewhere[6].

The *cw* CO_2 laser photosensitized (SF_6) dehydrochlorination of 1,1,1-trichlorethane was

performed in the set-up described in our previous paper[7]. The laser beam was focusséd with a parabolic mirror (f.l. 360 mm).

The reaction mixture used for the calculation of the Arrhenius parameters composed of sulfur hexafluoride, 2-chloropropane, 1,1,1-trichloroethane (all 1·4 kPa), and argon (36 kPa) was irradiated with a cw CO_2 laser (ref.[7]) having the following parameters: wavelength 10·59 μm (the P(20) line of the 00°1→10°0 transition), 5 W output and the calculated effective beam diameter 0·67 mm. The reaction progress was analyzed by means of the gas chromatography, IR spectroscopy, and mass spectrometry (ref.[7]).

2-Chloropropane (Fluka, AG Buchs), sulfur hexafluoride (Montedison, Milano, I.E.C. Standard), helium (Messergriesheim, Gumpolskirchen), and argon (Technoplyn, Prague) were commercial products. 1,1,1-Trichloroethane (Reactivue, Bucharest) was rectified for the fraction boiling at 74°C.

RESULTS AND DISCUSSION

The reaction mixture to be undergone the laser-powered homogeneous pyrolysis is composed of a reactant, sensitizer and an inert gas[1]. The addition of an inert gas alters hydrodynamic parameters and thermal conductivity of the mixture and ensures complete thermalization of the laser energy absorbed[8]. The temperature at which the pyrolysis of a reactant mostly progresses can be influenced by a few parameters of those the partial pressure of inert gas will be discussed first.

The dependence of temperature in the reactor upon molar ratio of helium experimentally found for the SF_6–He mixture is given in Fig. 1. There is a steady decrease
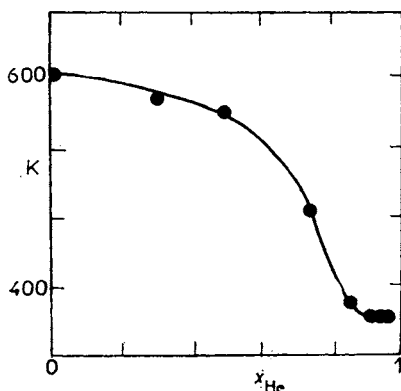

FIG. 1

Temperature T vs molar ratio of helium x_{He} dependence for the SF_6–He mixture at the position of the reactor $z = 12$ mm, $r = 4$ mm with 4 W laser output
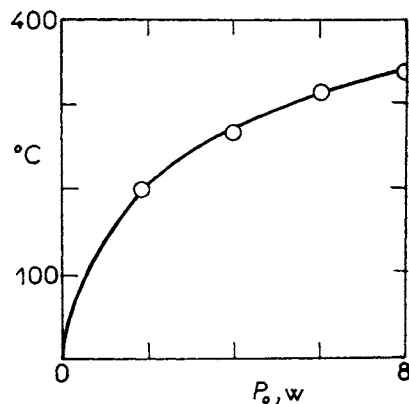
FIG. 2

Temperature T vs laser output P_0 dependence for the 0·8 kPa of SF_6 at the position of the reactor $r = 4$ mm, $z = 12$ mm

of temperature with increasing partial pressure of helium up to a certain value $(x_{He} = 0.9)$ from that no further alteration of temperature is observed when going to still higher partial pressure of helium. This allows to expect that thermal conductivity of the SF_6 (1·4 kPa)–inert gas (38·5 kPa) mixture is equal to that of the SF_6 (1·4 kPa)–reactant (1·4 kPa)– inert gas (35·7 kPa) mixture that was used for the study of the cw CO_2 laser-induced dehydrochlorination. The above presumption enables to compare the reactivity of two or more compounds in the reactant–sensitizer–inert gas system because the admixture of a reactant to the sensitizer–inert gas mixture does not change the distribution of temperature and the reactions progress separately under the same temperature conditions.

Other parameters that can produce alterations in the distribution of temperature in the laser photosensitized reactions are reactor configuration, sort of inert gas, laser output, effective laser beam diameter, and partial pressure of sensitizer. As for the first two variables, they were already discussed in our previous paper[6], where it was shown that suitable reactor configuration is vertical with that the distribution of temperature is symmetric along the laser beam and the minute particles formed in the course of the laser induced reaction are conveyed away from the entrance window. As for the sort of inert gas[6], reaction temperature and rate increase with decreasing thermal conductivity of inert gas in the order He, Ne, Ar, Kr and Xe. The high thermal conductivity of helium does not make this gas suitable for laser induced reactions since its thermal conductivity has to be compensated with high laser output.

The reaction rate of laser induced reactions is noticeably dependent on the laser output and effective beam diameter (intensity of radiation). Most reactions can be induced with focussed radiation of $2-8$ W output. The dependence of temperature in sulfur hexafluoride on the laser output covering this range is illustrated in Fig. 2. It is seen that temperature increases with increasing laser output. On the contrary, temperature is decreased with an increase of the effective beam diameter (Table I).

Absorptivity of the reaction mixture is also sensitive function of partial pressure of sensitizer. Hence, the temperature distribution is affected with partial pressure of sensitizer as well. Increasing absorptivity leads to the absorption on a shorter optical pathway, there increase the energy absorbed in a volume element and the hot zone temperature. The experimentally ascertained dependence of the temperature inside the reactor on the sensitizer concentration (Fig. 3) can be explained in a way that the initial increase of the temperature in a region of lower partial pressure of sensitizer is brought about with a progressive increase in a number of absorbed photons in the volume unit. In a region of high partial pressures of sensitizer all the energy can be understood as being absorbed in the close proximity of the entrance window. In such a case the distance between the measured position $(r = 4$ mm, $z = 12$ mm$)$ and the place directly heated by the radiation increases with increasing partial pressure of sensitizer, which would reflect the decrease of the temperature at the measured position.

The study of the aforementioned dependencies of temperature inside the reactor wherein the laser-photosensitized reaction occurs, on a number of variable parameters is helpful in understanding the rules that the reaction obeys. The reaction kinetics is treated considering the two, already commonly accepted models.

The first one[2,4] presumes the reaction to take place solely in a close proximity of the entrance reactor window at maximum temperature T_{max} defined as

$$T_{max} = T \ (r = 0, \ z = 0),$$ (1)

where r and z are the cell radius and length, respectively. The rate constant of laser induced reaction k_{max} occurring at the temperature T_{max} is obtained[2] from Eq. (2)

$$k_{max} = \frac{\alpha_0 \cdot T_{max}}{300\pi \cdot a^2 p_{300}} \cdot \frac{dR}{d \ln P_0},$$ (2)

TABLE I

T_{max} values for different effective beam diameter in SF_6/Ar mixture

a, mm[a]	T_{max}, K
0·3	2 492
0·4	2 404
0·5	2 338

[a] Calculated for reactor diameter 18 mm, optical absorption coefficient $0·032 \ mm^{-1}$, and laser output 4·9 W.
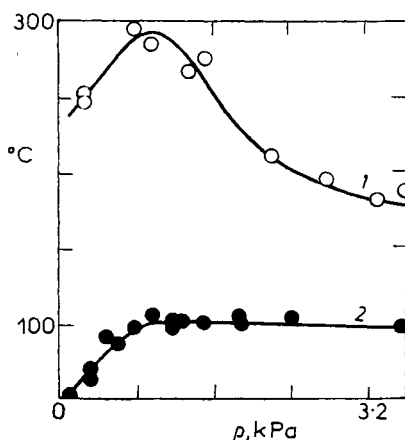

FIG. 3

Temperature T vs pressure or partial pressure of sensitizer dependence at the position of the reactor $r = 4$ mm, $z = 12$ mm for the SF_6 1 and SF_6–Ar mixture (total pressure 40 kPa) 2. Laser output 4 W.

where α_0 denotes optical absorption coefficient of the reaction mixture obtained by the measurement of the absorption of the radiation in the reactors long 11 and 16 mm, a the effective beam diameter, p_{300} the partial pressure of the reactant at 300 K, R the rate of the reaction studied, and P_0 the output corrected for the losses on the reactor entrance window. Calculation of the $dR/d \ln P_0$ was made from the plot $\ln R$ vs $1/P_0$ (Eq. 3, ref.[2])

$$\ln R = \frac{c_1}{P_0} + c_2 . \tag{3}$$

The second model[5] considers the laser-induced reaction to progress throughout the entire reactor volume at an effective temperature calculated on the ground of experimentally obtained rate constant and the Arrhenius parameters of a standard chemical reaction (Eq. (4))

$$k = A \exp \frac{-E_a}{RT_{eff}} . \tag{4}$$

Both approaches were taken to work out the cw CO$_2$ laser photosensitized (SF$_6$) dehydrochlorination of 1,1,1-trichloroethane, the reaction described in detail else-

TABLE II

Temperatures and rate constants of cw CO$_2$ laser-photosensitized dehydrochlorination of 1,1,1--trichloroethane

P_0 W	T_{max}[a] K	$\log k_{max}$[b] s^{-1}	T_{eff}[c] K	$\log k$ s^{-1}
3·2	1 773	6·19	663	−3·87
3·7	1 921	6·69	680	−3·32
4·2	2 062	6·83	689	−3·18
4·7	2 195	7·19	709	−2·76
5·2	2 324	7·30	717	−2·63
5·7	2 447	7·45	720	−2·42
6·2	2 567	7·72	725	−2·19
6·7	2 680	7·81	728	−2·09
7·2	2 792	7·89	747	−1·89
7·7	2 900	8·23	754	−1·64

[a] For calculation of T_{max} see ref.[7]. [b] Rate constants were obtained by the least squares treatment of the plot $\ln S/S_0 = -kt$, where S and S_0 are the glc peak areas of the reactant in time t and zero time, respectively. [c] Arrhenius parameters of the standard reaction, dehydrochlorination of 2--chloropropane, $E_a = 212$ kJ mol^{-1} and $\log A$ (s^{-1}) = 13·4 were taken from ref.[9].

where[7]. As a standard reaction we have chosen dehydrochlorination of 2-chloro-propane.

The T_{max}, T_{eff}, log k_{max} and log k are gathered in Table II and from those the Arrhenius parameters of the dehydrochlorination of 1,1,1-trichloroethane were calculated by the least squares treatment of the corresponding rate constant vs temperature plots.

The Arrhenius parameters provided by the first approach (T_{max}), i.e. $E_a = 164$ kJ mol^{-1}, log A (s^{-1}) $= 11 \cdot 0$, are lower than those reported for the conventional pyrolysis in the literature[8] $E_a = 227$ kJ mol^{-1}, log A (s^{-1}) $= 14 \cdot 0$. The values obtained via the second approach (T_{eff}) $E_a = 230$ kJ mol^{-1}, log A (s^{-1}) $= 14 \cdot 3$ match the literature data rather well. It thus turns out that the second, simpler approach is to be applied for the calculation of the Arrhenius parameters of further laser photo-sensitized reactions.

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