

CW CO₂ LASER PHOTOSENSITIZED DECOMPOSITION OF n-HEPTANEJosef POLA^a, Pavel KUBÁT^a, Josef VÍTEK^a, Marta FARKAČOVÁ^b and Antonín TRKA^c^a *Institute of Chemical Process Fundamentals,**Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát,*^b *Prague Institute of Chemical Technology, 166 28 Prague 6 and*^c *Institute of Organic Chemistry and Biochemistry,**Czechoslovak Academy of Sciences, 166 10 Prague 6*

Received March 22th, 1983

CW CO₂ laser (the P(34) line, 6.5 W output) induced and SF₆ (2.4 kPa)—sensitized decomposition of n-heptane (7.2 kPa) gives mainly ethylene. Propene, butene, ethane and methane are produced as well together with minor amounts of vinylacetylene, 1,3-butadiene, allene, n-butane, 1,4-pentadiene, pentene, and cyclopentadiene.

The product distribution corresponds to that obtained in conventional thermolysis of n-heptane performed at temperatures higher than 1 000°C. The inferences on the size and shape of the hot reaction zone are drawn on the basis of the measurement of temperature profiles in reaction cell.

The recently invented technique of CO₂ laser photosensitized decomposition¹⁻³ has quickly proved to be a tool for inducing thermal organic reactions with some features⁴⁻¹¹ unattainable by ordinary heat source. Different course of the CO₂ laser photosensitized reactions is currently assumed to be due mainly to the absence of heterogeneous reaction steps that cannot be obviated in conventional hot wall reactors. Depending on the CO₂ laser power the reactions may involve collisions of molecules to be decomposed with differently vibrationally excited sensitizer molecules and/or sensitizer molecules with a large excess of translational energy. Although the laser heating is spatially and temporally nonhomogeneous, the chemically reacting systems irradiated with modest CO₂ lasers and using a sensitizer with rapid vibration-translation relaxation time are considered⁹ to become homogeneous within a period of about 10⁴ times shorter than reaction times due to rapid mixing of reacting layers that is brought about by strong convection currents.

In this note we try to contribute to the knowledge of the cw CO₂ laser-sensitized reactions by studying the temperature profiles and the product distribution in cw CO₂ laser-induced and SF₆-sensitized decomposition of n-heptane. The study of the reaction itself was approached in the belief that it can offer some advantages over the conventional n-heptane pyrolysis so often studied for industrial purposes.

EXPERIMENTAL

A cw CO₂ laser operated at the P(34) line of the 00°1→10°0 transition with 6.5 W power was used for the irradiation of gaseous mixture of SF₆ sensitizer (2.4 kPa) and n-heptane (7.2 kPa). The experiments were carried out with a cylindrical glass tube of 10 cm path length and 3.6 cm

inner diameter fitted with NaCl windows and one P.T.F.E. stopcock. The laser beam was focussed with a Ge lens ($f. l. 25 \text{ cm}$) into the middle of the cell that was in vertical position, the laser beam entering its bottom. The samples for laser irradiation experiments were prepared by a standard vacuum-line technique. The reaction progress with the gaseous SF_6 -*n*-heptane mixture irradiated at measured intervals was monitored by infrared spectrometer Perkin-Elmer 621. The products were analyzed on a Chrom 3 gas chromatograph provided with a flame ionization detector, the separation of hydrocarbons being carried out on two different packed columns, namely 25% squalane on Chromosorb, and water-deactivated alumina, which was reported previously¹². For the identification of the decomposition products both the comparison of their retention times with those of standard compounds and the gas chromatography-mass spectrometry method was used.

The GC/MS system consisted of the PYE Unicam 104 gas chromatograph equipped with a packed column ($3 \text{ m} \times 3 \text{ mm id.}$, 25% squalane on Chromosorb) connected with the AEI MS 902 double focussing mass spectrometer (Associated Electric Industries, Manchester) by means of a steel capillary ($70 \text{ cm} \times 0.3 \text{ mm id.}$) and the Watson-Biemann separator. The best gas-chromatographic separation was achieved by the temperature programmed from 30 to 80 °C. The electron impact induced mass spectra were taken by the electron energy of 70 eV and the resolving power of 1000. The interpretation of the acquired mass spectra was aided by the standard mass spectra¹³. The quantitative analysis was done by peak area measurement (the precision of such a treatment corresponds¹⁴ to a standard deviation of about 3%).

Temperature measurements of the gaseous SF_6 -*n*-heptane mixture exposed to the cw CO_2 laser radiation was performed for different points inside the vertically positioned cell equipped with six thermocouples (jacket diameter 0.15 mm, Walzwerk Hettstadt) placed 0, 6, 12, 38, 63 and 88 mm (x) above the entrance bottom window. The distance of the thermocouples from the laser beam (r) passing through the cell and matching its axis varied from 0 to 18 mm. For the exact determination of the cw CO_2 laser beam path through the cell the identical path of the cw CO_2 laser beam with that of a He-Ne laser (HNA 50, Carl Zeiss, Jena) was settled.

The voltage on the individual thermocouples was recorded at the speed of 10 channels per s by means of the digital center Dynamco Systems (Chertsey) with an accuracy 0.05 mV. The results were fed into punched paper tape and evaluated by the EC 1033 computer.

Sulfur hexafluoride (Montedison Milano, I.E.C. Standard) was the commercial product, the purity of *n*-heptane donated from Chemické závody, Litvínov was checked by gas chromatography and found to be better than 99.5%.

RESULTS AND DISCUSSION

Mainly practical reasons have been unceasingly keeping the research on the thermal decomposition of *n*-heptane active for many years, since a knowledge of the distribution of the products afforded by the pyrolysis of this compound (and other unbranched alkanes) is indispensable to the design of pyrolytic facilities. The composition of the primary products of thermal decomposition of higher hydrocarbons was predicted as early as in 1943 by Kossiakoff and Rice¹⁵ who added the assumption of radical isomerizations to the Rice and Herzfeld theory¹⁶ of free radical reactions. Since that time other prediction of the initial product distribution was issued taking into account equilibria among all the possible isomers of higher hydrocarbon radicals¹⁷, and the product distribution at higher conversions was suggested to be

affected by reactions between higher olefinic hydrocarbons and chain propagating radicals, mainly hydrogen atoms¹⁸.

The pyrolysis of *n*-heptane taking place at temperatures 550–750°C affords^{14,18,19} the following major product distribution: methane (15–18%), ethylene (30%), ethane (13–16%), propene (15%), butene (10–12%) and pentene (7%). The product distribution little alters¹⁵ depending upon the temperature, quality of the inner surface of reactor and residence time.

Our cw CO₂ laser-photosensitized experiments afford a high yield of ethylene, together with some quantities of propene, methane, ethane, and butene. Minor amounts of vinylacetylene, 1,3-butadiene, allene, *n*-butane, 1,4-pentadiene, pentane, cyclopentadiene, and traces of acetylene were detected, too. The amounts of major products gathered in Table I are quite dissimilar to those obtained with the static¹⁸ or the flow^{15,19} pyrolysis experiments performed in the temperature range 590 to 760°C. The high yield of ethylene obtained with the photosensitized decomposition resembles that for *n*-heptane flow pyrolysis²⁰ in nitrogen diluent at the temperatures as high as 1100°C. However, the product distribution of this high temperature flow pyrolysis is strongly dependent on the *n*-heptane conversion and yields propene and acetylene in comparable quantities. None of these two features is observed with CO₂ laser photosensitized decomposition of *n*-heptane which gives only traces of acetylene and shows no alteration of the product distribution with the degree of *n*-hexane conversion (Table I).

The specific features of the CO₂ laser sensitized decomposition have to be discussed in connection with the temperature profiles determined for the SF₆-*n*-heptane mixture (Fig. 1) after the irradiation not exceeding 3 s. During this period the decomposition progresses up to a few percent conversion and temperature seems to grow to a constant values (Fig. 2). The measurement of the absorption of the laser beam

TABLE I
Major product distribution at different conversions

n-Heptane conversion ^a %	mol/mol of n-heptane decomposed				
	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈
10	0.70	0.13	2.3	0.38	0.08
37	0.65	0.10	2.4	0.40	0.11
65	0.70	0.08	2.6	0.41	0.10
89	0.70	0.13	2.6	0.35	0.09

^a The irradiation time needed for the decomposition to achieve 100% conversion reaches 100 s.

by the SF_6 -*n*-heptane mixture in a cylindrical cell of 1.4 cm length and 3.6 cm diameter revealed that almost 30 percent of radiation is transmitted through the sample. These conditions do not exactly relate to the conditions in the cell wherein the *n*-hexane decomposition was studied, there may be nevertheless possible that $T(r=0, x=12)$ parameter is affected not only by translationally hot molecules but also by direct radiation. This is obviously not the case for other measured points inside the cell.

The highest temperature T was found for the points (r, x, mm) 220°C (0,12), 130°C (4,0) and 180°C (4,6). Taking into account the temperature profiles illustrated in Fig. 1, one is tempted to conclude that the *n*-heptane decomposition, that demands temperatures by a few hundreds degrees higher, must occur in a probably cylindrically shaped volume with its axis identical with that of the cell and positioned between the entrance window and the first layer of thermocouples ($x=12$). The diameter of this reaction volume has to be smaller than 8 mm and its length less than 12 mm. Keeping in mind

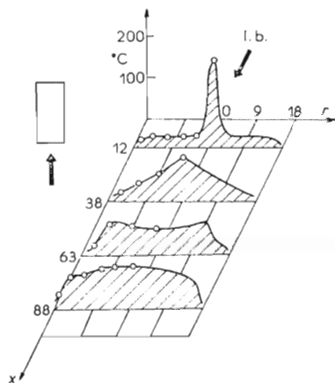


FIG. 1

The temperatures of the SF_6 (2.4 kPa) — *n*-heptane (7.2 kPa) mixture irradiated with the *cw* CO_2 focussed laser beam (the P(34) line, 6.5 W output) as a function of the radius (r) and the length (x) (both in mm) of the vertically positioned cylindrical cell after 3 s irradiation

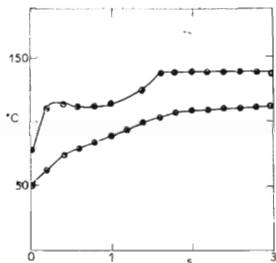


FIG. 2

Dependence of the temperature T inside the irradiated SF_6 -*n*-heptane mixture on the irradiation time t . The conditions are identical as in Fig. 1, the upper curve and lower curve relates to the points (r, x) (4,0) and (4,6), respectively

that the laser beam is partly transmitted after the passage through the volume of 1.4 cm path length, the SF₆ molecules inside the reaction volume can be assumed to possess some content of vibrational energy that can be utilized in their collisions with *n*-heptane molecules for the *n*-heptane decomposition to occur.

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Translated by the author (J. P.).