cw CO_2 LASER PHOTOSENSITITED DECOMPOSITION OF CYCLOHEXANE

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The *cw* CO_2 laser photosensitized (SF_6) decomposition of cyclohexane affords high yields of ethylene and butadiene along with minor amounts of propene, methane and ethane. The products distribution is very slightly altered with the reaction progress. The process is shown to have practical importance, and its course different from conventional pyrolysis is inferred to come from the absence of surface effects.

It was more than 40 years ago that the study of the thermal decomposition of cyclohexane admitted[1] the involvement of a radical chain mechanism. Since that time further interest in this reaction was stimulated by mainly practical reasons[2-7] and consisted in the investigation of the dependence of the distribution of the pyrolytic products upon the reaction conditions. An abudance of these previously published data[2-6] have been carried out with possible contributions from surface effects, and it was only recently that thermal behaviour of cyclohexane was studied by the shock tube technique ensuring the reaction to occur strictly in a homogeneous phase. The mechanism of this cyclohexane decomposition has been determined[8] to involve isomerization of cyclohexane to 1-hexene and ensuing decomposition of the latter compound, the rationale not identical with that accepted[7] for the decomposition in which surface effects are possibly involved. The homogeneous decomposition of cyclohexane was studied only for the extremely small extent of reaction and did not give an answer whether its product distribution at higher conversions differs from that of the decomposition in which surface effects are possibly involved.

The growing usage of the technique of the infrared laser powered homogeneous pyrolysis[9-11] (LPHP) for the improvement of our understanding[12-18] of surface effects in gas-phase reactions stems form the fact that the technique is adaptable to general application. In the course of our studies on the infrared laser driven homogeneous pyrolysis of hydrocarbons[19-21] we paid in this note attention to the LPHP of cyclohexane in conditions similar to those concerned in the industrial production of olefins.

EXPERIMENTAL

The experimental techniques, a *cw* CO_2 laser, the apparatus and the products analysis used in this work were described elsewhere[19]. The concentration of sulfur hexafluoride and cyclohexane in their gaseous mixtures irradiated with CO_2 laser was determined on the basis of the knowledge of their pressures and infrared absorptivities at 987 cm^{-1} ($\nu_2 + \nu_6$) and 1 445 cm^{-1} (ν_{14}), respectively.

Sulfur hexafluoride (Montedison, Milano, I.E.C. Standard) and cyclohexane (International Enzymes Ltd., Windsor, *p.a.*), were commercial products used without purification.

RESULTS AND DISCUSSION

The *cw* CO_2 laser (the P (34) line of the 00°1→10°0 transition, laser power 7·5 – 8 W) photosensitized decomposition of cyclohexane was investigated for total pressures of gaseous mixtures of cyclohexane with sulphur hexafluoride sensitizer 6 – 13 kPa and concentration of sulphur hexafluoride 18 – 55 mol %. Typical reaction conditions are given in Table I. This decomposition of cyclohexane yields mainly ethylene, 1,3-butadiene and minor amounts of propene, methane and ethane. These products distribution does not depend on the SF_6 concentration within the range studied and little alters with conversion (Fig. 1).

High yields of ethylene and butadiene and their almost constant values for all the extent of the reaction studied (5 – 95% conversion) are unique features of the laser-induced process, since so high yields of both products are not obtained at temperatures between 600 – 800°C in reactors with possible involvement of surface effects wherein[4,7] the yields are markedly affected with conversion.

The similar yield of ethylene can be achieved[3] in conventional pyrolysis only at temperatures as high as 1 000 – 1 200°C. Under these conditions 1,3-butadiene is, however, produced in amounts by a factor of 1·2 times lower than in the laser-driven process and acetylene that was not detected in the laser process at all is formed in significant quantities.

Assuming the results on the laser-driven homogeneous decomposition of 2-nitropropane[22] conducted under similar conditions, the effective temperature in the laser driven decomposition of cyclohexane can be considered as ~ 700°C. Our measurements[19,23] of temperature profiles inside the *cw* CO_2 laser irradiated and vertically positioned cell filled with sulfur hexafluoride revealed that addition of an excess of helium results in a decrease of temperature by a few hundreds degrees. Similar addition of helium (28 kPa) to the mixture of SF_6 with cyclohexane (total pressure 12 kPa, 55 mol % SF_6) decreases the yield of methane and ethylene and increases the yield of 1,3-butadiene. This effect is rather small, but valid for a broad extent of reaction (Fig. 2). Estimating the effective temperature in helium-diluted cyclohexane–SF_6 mixture as about 300 – 400 °C and considering significantly higher yields of ethylene and 1,3-butadiene compared to conventional pyrolysis at these temperatures[4] one has to admitt the unusually high yields of both products to originate from the absence

TABLE I

Representative runs of *cw* CO_2 laser photosensitized decomposition of cyclohexane

Components	Total pressure kPa	mol % SF_6	Irradiation time, s	Conversion %
C_6H_{12} SF_6 —	10	18	60	6
C_6H_{12} SF_6 —	9·8	24	500	82
C_6H_{12} SF_6 —	9·7	33	140	70
C_6H_{12} SF_6 —	9·3	50	40	39
C_6H_{12} SF_6 He	40	55[a]	5	4
C_6H_{12} SF_6 He	40	55[a]	200	50

[a] He not considered.

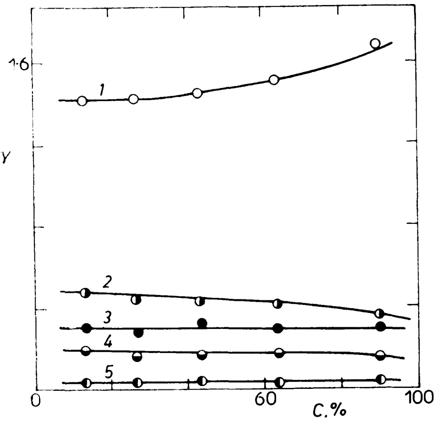

FIG. 1

The dependence of the product distribution upon conversion (*C*) in the *cw* CO_2 laser photosensitized decomposition of cyclohexane. Curves *1*—*5* relate in the given order to ethylene, 1,3-butadiene, methane, propylene, and ethane. The yield (*Y*) is given in mol per mol of C_6H_{12} decomposed

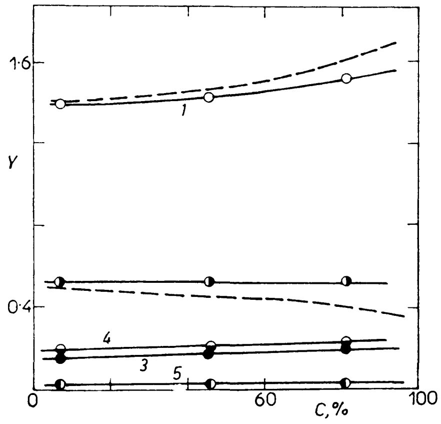

FIG. 2

The dependence of the product distribution upon conversion (*C*) in the *cw* CO_2 laser photosensitized decomposition of cyclohexane in the presence of helium. Curves *1*—*5* relate to the same products as in Fig. 1 and dashed curves are taken for the sake of comparison from Fig. 1. The yield (*Y*) is given in mol per mol of C_6H_{12} decomposed of surface effects. This inference also suggests that no production of acetylene in the laser-driven process in the absence of He is consistent with the fact that the formation of this compound occuring in conventional pyrolysis at temperatures higher than 1 000°C by the consecutive decompositions of 1,3-butadiene, propene, and ethylene is facilitated by reactor surfaces.

The laser photosensitized decomposition of cyclohexane is advantageous over conventional pyrolysis of this compound due to the almost invariable product distribution with conversion, better yields of important ethylene and butadiene, lower yields of less valuable methane and due to the fact that no heavy pyrolytic oils or coke were observed to be formed. This note thus reveals not only the effect of the absence of the surface effects on the cyclohexane decomposition course, but also shows the laser induced pyrolysis to have certain practical capabilities.

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