LASER DRIVEN PYROLYSIS OF n-ALKANES

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CW CO₂ laser photosensitized (SF₆) homogeneous pyrolysis of n-alkanes (C₅--C₇) affords almost twice higher yield of important ethylene compared to conventional pyrolysis in tubular reactors. No production of heavy pyrolytic oils, resins or coke and very small alteration of the pyrolytic distribution with the conversion are other advantages of the laser process that can be ascribed to the absence of in conventional reactors important surface reactions.

A knowledge of the product distribution in the hydrocarbon pyrolysis is needful to the design of pyrolysis facilities and kept the research on the thermal decomposition of hydrocarbons very active. An abundance of previously published data involves, however, the surface effects that have a pronounced influence upon the pyrolysis course owing to the possibility for many types of reactions stages to occur on reactor surfaces¹⁻³.

Despite that surface effects can be made less apparent with specially designed reactors⁴, reactors with passivated walls, or by using an inert diluent³, their complete elimination is enabled only by the shock tube⁵ or infrared laser techniques.

Recently, the high temperature pyrolysis of saturated hydrocarbons was achieved by infrared laser gas breakdown and shown to efficiently produce acetylene and hydrogen with only minute amounts of ethylene that resonantly absorbed the laser radiation and decomposed into carbon⁶. In the infrared laser-powered homogeneous pyrolysis (LPHP) technique⁷⁻⁹ the compounds which do not themselves absorb laser radiation are activated by collisional energy transfer from an unreactive, I.R. radiation absorbing gas as SF₆ or SiF₄. Despite that the usefulness of this technique consisting in obviating reaction components that occur on hot reactor walls was already demonstrated, the technique was not to our knowledge applied to any reaction of industrial importance.

In this paper we use $cw CO_2$ laser to perform "wall-less" SF₆-sensitized pyrolysis of n-alkanes C_5 — C_7 and show this procedure to afford much higher yield of important ethylene than conventional pyrolysis in tubular reactors. Additional advantages of the laser-powered pyrolysis of n-alkanes are that it does not yield heavy pyrolytic oils, resins and coke and that the distribution of pyrolytic products is almost not affected with conversion.

EXPERIMENTAL

Experiments were carried out in a reaction cell as a part of experimental set-up shown in Fig. 1. The cell consisted of a cylindrical glass tube o 10 cm length and 3.6 cm inner diameter fitted

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with NaCl windows and three values. A $cw \operatorname{CO}_2$ laser operated at the P(34) line of the $00^\circ \rightarrow 10^\circ 0$ transition with 7 W power was used for the irradiation. The laser power was measured with a Coherent Model 201 powermeter. The laser beam was focussed with a Ge lens (f.l. 25 cm) at the center of the cell. The sample for the laser irradiation experiments — gaseous mixtures of hydrocarbon and sulfur hexafluoride (total pressure 5-13 kPa, concentration of sulfur hexafluoride sensitizer 15-60 mol %) were prepared by a standard vacuum-line technique and the concentration of both components was checked by infrared spectrometer Perkin-Elmer 621 using the absorption at 1 380 cm⁻¹ (n-alkanes) and 987 cm⁻¹ (sulfur hexafluoride). The reaction progress was monitored using a sampling valve¹⁰ coupled with a Chrom 3 gas chromatograph provided with a flame ionization detector. The separation of products was carried out on 25% squalane on Chromosorb and water-deactivated alumina¹¹. For the identification of the gas chromatography-mass spectrometry method was used¹². The quantitative analysis was done by peak area measurement (the precision of such a treatment³ corresponds to a standard deviation of about 3%).

n-Pentane (Jenapharm), n-hexane (Lachema, Brno), n-heptane (Chemické závody, Litvínov), all pure and sulfur hexafluoride (Montedison Milano, I.E.C. Standard) were commerical products.

RESULTS AND DISCUSSION

The pyrolysis of straight-chain hydrocarbons in tubular reactors between 600 and 800°C gives a complex mixture of products among them ethylene is the most important^{13,14}. The composition of primary products of the thermal decomposition of hydrocarbons was predicted as early as in 1943 by Kosiakoff and Rice (ref.¹⁵) who added the assumption of radical isomerization to the Rice and Herzfeld theory¹⁶ of free radical reactions. The prediction of the initial product distribution was modified by Murata and coworkers¹⁷ who considered equilibria among all the possible isomers of higher hydrocarbon radicals. As for the product distribution at higher conversions, it is viewed¹⁴ to be affected by reactions between higher olefinic hydrocarbons and chain propagating radicals, mainly hydrogen atoms. The relative



FIG. 1

Apparatus used for laser-driven pyrolysis of n-alkanes. $a cw CO_2$ laser, b beam splitter, c reaction vessel, d powermeter, e gas reservoir, f sampling valve, g vacuum line, h gas chromatograph

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TABLE I

Comparison	of the	main	product	distribution	(% wt)	in	conventional	(C)	and	laser-driven	(L)
pyrolysis of	n-alkar	nes									

Dec de staf	n-Pe	ntane	n-He	exane	n-Heptane	
Products	С	L	С	L	С	L
Methane	13-16	12	14 17	9-12	12	8-10
Ethylene	30-35	45-59	33-41	5764	37-43	63-75
Ethane	7-9	4	7	5	6-8	3-6
Propene	15-16	19-22	14-18	16-22	15-16	13 - 20

20

C

" Data on conventional pyrolysis (780°C) taken from ref.¹³.





The dependence of the product distribution upon conversion in the laser-driven pyrolysis of n-pentane (a), n-hexane (b), and n-heptane (c). Curves 1-4 relate in the given order to ethylene, methane, propene, and ethane. The yield is given in mol per mol of n-alkane decomposed



80

%

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yields of the main products at temperatures between 600 and 800°C do not appreciably alter with temperature and quality of the inner surface. They are, however, affected with the residence time²⁴. High conversions favor methane and ethylene and disfavor ethane, propylene, butene and pentene.

The laser driven SF₆-sensitized pyrolysis of straight chain hydrocarbons (n-pentane, n-hexane and n-heptane) affords ethylene, propene, methane, ethane and traces of butenes and acetylene. Mass balance performed by GC coupled with sampling valve and based on the determination of absolute amounts of the above products revealed that the formation of other possible products, as heavy pyrolytic oil and tar is insignificant (<1%). The product distribution does not depend within the range studied on the SF₆ concentration. The SF₆ concentration controls, however, the irradiation time necessary to drive the pyrolysis to completion. The time varies for the SF₆ concentrations studied (15-60 mol%) from tens seconds to tens minutes. Comparing the yields on the laser photosensitized pyrolysis with the literature data on the surface pyrolysis (Table I) one sees that all the main products but ethylene are produced in similar quantities. The yield of ethylene is almost twice higher in the laser-induced process and resembles that for the flow pyrolysis of hydrocarbons carried out in nitrogen diluent at temperatures higher than 1 100°C (ref.¹⁸).

Both processes have to bear, however, different features. While the product distribution in the high temperature surface pyrolysis is strongly dependent on the conversion and yields propene and acetylene in comparable quantities, the distribution of products in the laser-driven pyrolysis, the process occurring in a small volume (the hot zone) of the reactor¹² and controlled by convection currents^{8,19,20}, does not appreciably alter with the reaction progress (Fig. 2) and gives only traces of acetylene yields lower than 1%). Moreover, in the laser pyrolysis no heavy pyrolytic oils or coke, the formation of those is so pertinent to pyrolysis carried out in hot wall reactors, were produced in noticeable quantities.

The contribution thus reveals that no involvement of surface effects in the thermal decomposition of n-alkanes has a tremendous impact on the yield of important ethylene, which shows the laser-driven pyrolysis of n-alkanes to have at least some practical capabilities.

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