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UV Laser Activation of Alkanes

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UV laser irradiation of mixtures of n-heptane with acetophenone, benzaldehyde or nitrobenzene stimulates C—C bond breaking in n-heptane and a dehydrocyclization reaction occurs to form alkenes, benzene and toluene; mixtures of cyclohexane with nitrobenzene give ethylene, butene and benzene as the major products.

The advantages of lasers over lamps for chemical applications has been reviewed by Schäfer.[1] IR laser irradiation has been used to induce thermal cracking of hydrocarbons.[2] We now present a method for the activation of the C—H and C—C bonds in alkanes by pulsed UV laser irradiation (KrF excimer laser, wavelength $\lambda = 248$ nm, pulse duration $\tau = 20$ ns).

Saturated hydrocarbons do not absorb at the KrF laser operating wavelength, so mixtures of alkanes with compounds showing intense absorption at the operating wavelength (*e.g.* acetophenone, benzaldehyde, nitrobenzene and biphenyl) were subjected to irradiation. We propose calling these compounds 'sensitizers' although, of course, they are not classical photosensitizers. n-Heptane and cyclohexane were used as substrates. The solutions were irradiated in a glass cell through a quartz window. A uniform patch with dimensions 3×8 mm was formed in the sample. Liquid and gaseous products resulting from the conversion of n-heptane and cyclohexane were analysed by gas chromatography–mass spectrometry.

All the sensitizers appear to be stable under the experimental conditions. No products of the transformation of acetophenone, benzaldehyde, nitrobenzene or biphenyl are detected apart from the formation of carbon films and solid carbon particles (less than 0.01% of the mass of the sensitizer).

The main products of n-heptane conversion are C_2–C_6 alkenes and aromatic hydrocarbons benzene and toluene. Hydrogen and saturated C_2–C_5 hydrocarbons are formed in smaller amounts, together with traces of methane and C_3–C_5 dienes. The composition of the products obtained from n-heptane does not depend on the number of pulses, *N*. For example, the composition of the products and their quantum yields, determined according to ref. 3, are given in Table 1. It should be noted that the composition and yields of the products obtained by irradiation are independent of the experimental conditions (saturation of the solution with argon or the use of argon or air atmosphere).

Fig. 1 shows that the yields of the products increase with energy density E_s. Extrapolation of the plots allows one to estimate approximately the threshold values of the energy density required for the beginning of n-heptane conversion (about 125 mJ cm^{-2}).

Experiments showed that an increase in the concentration of the sensitizer resulted in an increased yield of alkenes and aromatic hydrocarbons (*e.g.* mixture of n-heptane and nitrobenzene, Fig. 2).

Ethylene, butene and benzene appear to be the main products obtained from cyclic saturated hydrocarbon–cyclohexane upon UV laser irradiation. Unlike n-heptane, for which a rise in E_s increases the yields of aromatic hydrocarbons in comparison with alkenes (Fig. 1), an increase of E_s in the case of cyclohexane leads to the favourable formation of alkenes (Fig. 3). From Fig. 3 one can evaluate approximately the threshold value E_s leading to the decomposition and dehydrogenation of cyclohexane (about 150 mJ cm^{-2}).

Table 1 Yields of reaction products from n-heptane and general quantum yields ϕ for an experiment using 35% (by mass) nitrobenzene ($E_s = 366$ mJ cm^{-2}, $N = 10\,000$, complete pulse energy $E = 33$ mJ)

Reaction product	Yield/mol per 100 mol converted n-heptane	$10^3 \times \phi$/molecule per quantum
H_2	112	175.0
CH_4	0.5	0.7
C_2H_4	39	61.0
C_2H_6	14	21.8
C_3H_6	33	51.5
C_3H_8	6	9.1
C_3H_4	2	3.5
C_4H_8	17	26.0
C_4H_{10}	2	3.7
C_4H_6	1	1.4
C_5H_{10}	9	13.4
C_5H_{12}	1	1.8
C_5H_8	0.3	0.5
C_6H_{12}	3	4.6
C_6H_6	30	46.8
C_7H_8	21	32.2
Total	290.8	453

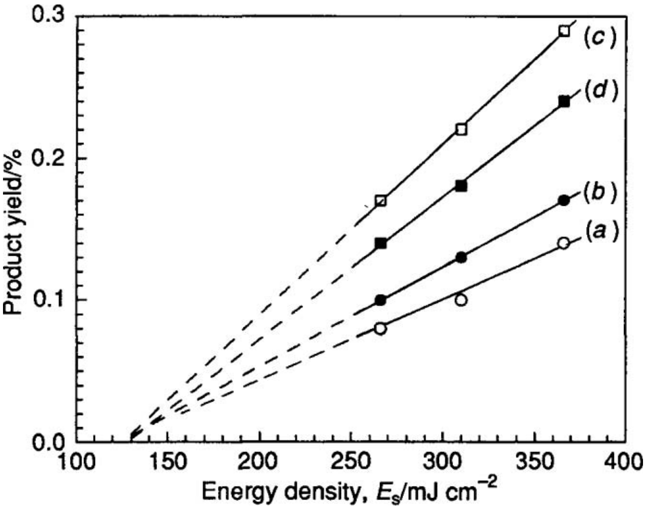

Fig. 1 Yields of main products *vs.* energy density for n-heptane conversion [35% (by mass) nitrobenzene, number of pulses $N = 10\,000$]; (*a*) ethylene, (*b*) propylene, (*c*) benzene, (*d*) toluene

The extent of cyclohexane conversion is appreciably lower than that of n-heptane. For example, at $N = 10\,000$ and $15\,000$, the conversion of cyclohexane is 0.3 and 0.45%, respectively, *vs.* 1.22 and 1.8% for n-heptane [in experiments using 35% (by mass) nitrobenzene solution and $E_s = 366$ mJ cm^{-2}].

It should be noted that additives had no effect on the

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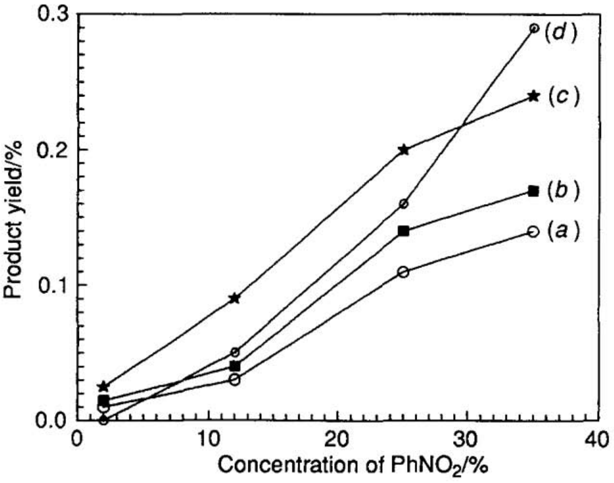

Fig. 2 Dependence of yields of main products on the concentration of nitrobenzene for n-heptane conversion (E_s = 366 mJ cm^{-2}, N = 10 000); (*a*) ethylene, (*b*) propylene, (*c*) benzene, (*d*) toluene

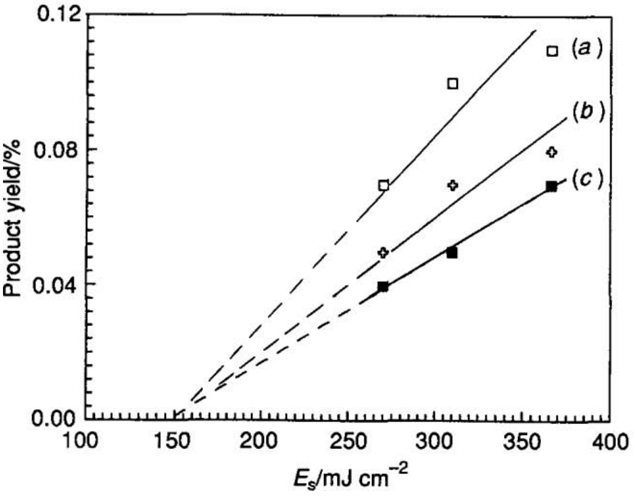

Fig. 3 Product yields *vs.* energy density for cyclohexane conversion [35% (by mass) nitrobenzene, N = 10 000]; (*a*) ethylene, (*b*) butene, (*c*) benzene

initiation of the radical conversion. In fact, irradiation of n-heptane, containing 4% $CHCl_3$ in addition to nitrobenzene, does not change either the yields or the composition of products. A slight increase in the yield of butene in dibutyldisulphide and benzene when benzoyl peroxide is added may be explained by the decomposition of the additives themselves.

The three sensitizers, acetophenone, benzaldehyde and nitrobenzene exhibit similar results. Biphenyl, while possessing the greatest absorbance of all the compounds under consideration,[4] appeared to be a bad sensitizer. The main reason for its weak sensitizing activity may be explained by the fact that a considerable part of the energy absorbed during UV irradiation is spent on the rotation of the phenyl rings around the C—C bond. This is supported by the fact that 2,2′-bipyridyl, which also undergoes such a rotation, behaves as a weaker sensitizer than its structural analogue *o*-phenanthroline,[5] in which rotation is impossible.

It is difficult to estimate correctly the temperature in the very thin layer of liquid where the laser beam is absorbed, owing to the complexity of calculating the redistribution of energy to heat the surrounding liquid and the percussion wave. However, the observed composition of the reaction products (and, in particular, the absence of acetylene) and the knowledge of the temperature interval for the formation of the products allows us to suggest that the temperature in the region of the laser beam does not exceed 1000 °C.

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