THE IR LASER STIMULATED DECOMPOSITION OF 1,3-BUTADIENE

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Gaseous 1,3-butadiene (pressure range 600–700 Torr) gives under irradiation with *cw* CO_2 laser (output power 18 W) products of dimerization and decomposition – 4-vinylcyclohexene, 1-butene and aromatic hydrocarbons. The observation indicates radical mechanism of the decomposition and manifests importance of the absorbed energy transfer through intermolecular collisions.

The possibility of enhancing[1-3] and inducing[4-7] chemical reactions using excitation of infrared lasers is currently of great interest since specific reaction channels otherwise unattainable by classical chemical procedures can be achieved. If thermalization of the energy absorbed[8-10] can take place, pyrolytic decomposition of compounds may be investigated, too.

Herein we wish to report on the behaviour of 1,3-butadiene exposed to the focused high-density irradiation with continuous wave CO_2 laser; the conditions used (pressure range of the compound 600–700 Torr) suggest rather thermal than selective reaction of 1,3-butadiene.

EXPERIMENTAL

The continuous wave CO_2—N_2—He laser operating in the 935 cm^{-1} wavenumber range was used for irradiation experiments. It consisted of a 2 m long (water cooled) discharged glass tube with two Brewster-angle sodium chloride windows and was fitted with gas inlet and pump outlet ports and a cavity consisting of two germanium mirrors at 2·5 m distance. The output coupling was achieved by a semitransparent mirror of 85% reflectivity. The discharge through a flowing gas mixture of CO_2, N_2, and He (1 : 2·5 : 10) was maintained (at total pressure about 10 Torr) by a stabilized power supply. The laser was operated at 18 kV and 40 mA with approximately 18 W output power.

The apparatus consisted of a 5 ml two-necked vessel, a 20 cm long distillation column packed with metal helices, an irradiation cell and a condenser cooled by dry ice-ethanol mixture. The irradiation cell was a glass tube equipped with two sodium chloride windows at each end and with four tubings, two of them being connected to a vacuum source and a manometer, the other two served for the cell interconnection between the distillation column and the condenser. During irradiation butadiene was distilled under reduced pressure (the pressure of butadiene being 600–700 Torr) from the 5 ml vessel, through the column into the cell and then the vapour condensed in the cooler was let to drop back into the 5 ml reservoir through a cooled tubing connected to the second vessel neck.

1,3-Butadiene was better than 99% purity as checked by gas–liquid chromatography.

RESULTS AND DISCUSSION

The analysis of the reservoir content after the irradiation by gas–liquid chromatography and mass spectrometry showed (Table I), besides of unchanged 1,3-butadiene, the presence of 1-butene, 4-vinylcyclohexene and aromatic hydrocarbons as benzene, toluene and alkyl- and alkenylbenzenes, indenes and naphthalene. These aromatic end products determined are similar to those which appeared in classical pyrolysis of butadiene. Thus, the low-temperature (about up to 650°C, the residence times with dynamic pyrolytic systems being lower than 1 second) pyrolysis of 1,3-butadiene yields[11–13] the product of Diels–Alder reaction – 4-vinylcyclohexene, while the pyrolysis performed at higher temperatures leads to the cracking of butadiene. When low pressure of butadiene is used[14] (<30 Torr) or butadiene is diluted with inert gas[15–18] the chief products are acetylene or ethylene, when butadiene is exposed[19,20] to the temperature at higher pressure (>100 Torr) mainly aromatic compounds are formed. As far as the pyrolysis carried out at atmospheric pressure of butadiene is concerned, 4-vinylcyclohexene is a major product at temperature below 600°C, and mainly aromatic compounds appear at temperatures above 600°C (ref.[21]). On the basis that the both types of products are formed by the laser irradiation we can therefore guess the temperature in the irradiation zone to be higher than 600°C.

Our results indicate the thermalization of the laser energy absorbed due to intermolecular collisions. The aromatic compounds appear to be formed by a radical

TABLE I

The IR Laser Stimulated Reaction of 1,3-Butadiene

Product[a]	Molar ratio[b]	Product	Molar ratio[b]
1-Butene	0·157	Styrene	0·024
Benzene	0·176	Indene	0·016
Toluene	0·082	1-Methylindene	—[c]
4-Vinylcyclohexene	0·082	3-Methylindene	—[c]
Ethylbenzene	—[c]	Naphthalene	0·011
Xylenes	—[c]		

[a] Tar and minute amounts of light gases were not identified. [b] Mol/mol of 1,3-butadiene decomposed. [c] Less than 0·006.

mechanism, the main component of the reaction system being $CH_2{=}CH^{\bullet}$. This seems to be supported by a similar benzene-to-toluene ratio in the pyrolysis (2·63, ref.[20]) as well as in the laser experiment (2·15, Table I). The formation of 1-butene and aromatic hydrocarbons obviously proves the presence of hydrogen radicals in reaction zone. 4-Vinylcyclohexene likely originates from thermal concerted[22] process.

In attempting to irradiate under similar conditions 4-vinylcyclohexene and 1,5-cyclooctadiene we have failed to observe any change with these comoounds; therefore, we can suggest that neither 4-vinylcyclohexene nor 1,5-cyclooctadiene play a role as an intermediate product during the laser experiment with 1,3-butadiene. We have to point out a crucial difference between the results presented here and those published in papers[23,24] where solely acetylene or mainly ethylene are reported to arise from 1,3-butadiene by irradiation emitted by CO_2 laser. However, it seems difficult to explain this difference at the present time.

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