

**CO₂ LASER PHOTSENSITIZED DEHYDROBROMINATION
OF BROMOETHANE AND 1-BROMOPROPANE.
A HOT-TUBE RADICAL-CHAIN REACTION
WITH MOLECULAR MECHANISM**

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Contrary to the gas-phase hot-tube reaction taking place by a blend of a molecular and radical-chain mechanism, the cw CO₂ laser induced dehydrobromination of bromoethane and 1-bromopropane occurs by only a molecular mechanism which is substantiated with reaction rates and products in the absence and the presence of radical-chain inhibitor (propene) and in the presence of chloroethane. The results point out the importance of hot walls for the initiation of radical-chain dehydrobromination.

The thermal gas-phase dehydrobromination of bromoethane and 1-bromopropane in hot surface vessels proceeds by a blend of a molecular and radical-chain mechanism and its reaction rate depends upon the reactor surface to volume ratio and the presence of radical-chain inhibitors (propene, cyclohexene)¹⁻⁵. The pyrolysis of chloroethane is accelerated with the addition of bromoethane². The total rate of the co-pyrolysis in the presence of cyclohexene is, on the other hand, equal to the sum of the decomposition rates of both compounds. It is therefore viewed² that chloroethane undergoes dehydrochlorination by a molecular mechanism while dehydrobromination of bromoethane progresses by a blend of a molecular and radical-chain mechanism, the latter dominating, but losing its significance in the presence of radical-chain inhibitors.

The important effect of the reaction vessel surface upon the dehydrobromination of bromoethane and 1-bromopropane led us to examine the reaction under the conditions eliminating this effect. Continuing our study of the laser-powered homogeneous pyrolysis (LPHP, ref.⁶) of halogenosubstituted hydrocarbons, we attempt in this paper to answer whether the radical-chain mechanism of the dehydrobromination of both the above compounds can be suppressed in favor of a molecular mechanism when the reaction is conducted strictly in the gas-phase. If so, the results here presented would show a CO₂ laser as a tool for avoiding free radical reactions not only with dehydrochlorination of chlorinated hydrocarbons^{7,8} but with dehydrobromination of brominated hydrocarbons as well.

EXPERIMENTAL

The apparatus used to study the dehydrobromination of bromoethane and 1-bromopropane was described earlier⁸. The vertically positioned tube-like reactor (inner diameter 36 mm, length 100 mm) equipped with two NaCl windows contained the mixture of SF₆ sensitizer (1.4 kPa), bromoethane or bromopropane (1.4 kPa) with or without chloroethane (1.4 kPa) or propene (0.7 kPa), and argon; total pressure being 40 kPa.

The mixture was irradiated with a *cw* CO₂ laser (ref.⁹, 4 W output, the P (20) line of the 00°1→10°0 transition, 10.59 μm) the beam of that was focussed by a Ge lens (f.l. 100 mm) 20 mm behind the reactor entrance window. Sulfur hexafluoride (Montedison, Milano, I.E.C. Standard), argon (Technoplyn, Prague), bromoethane (Lachema, Brno) and 1-bromopropane (Reagkhim, Moscow) were used without purification.

The progress of the dehydrobromination with gaseous mixtures irradiated at measured intervals was monitored using a technique (sampling valve coupled with Willy Giede gas chromatograph equipped with flame ionization detector) described in our previous paper⁸. The reaction rate of the dehydrobromination, *k*, represents a spatial average over the vessel volume and was obtained as first-order rate constant

$$k = \frac{1}{t} \cdot \ln \frac{S_0}{S}, \quad (1)$$

where *S*₀ and *S* designate the glc peak areas of reactant at the beginning of the reaction and time *t*, respectively.

The gas chromatographic analysis of the reaction was carried out on 10% Squalane on Chromosorb W. For the identification of the decomposition products both the infrared spectroscopy (Specord model 75 IR spectrometer) and gas chromatography were used.

Computational procedure used for the estimation of the temperature distribution inside the vessel irradiated with laser beam was reported earlier⁹⁻¹¹.

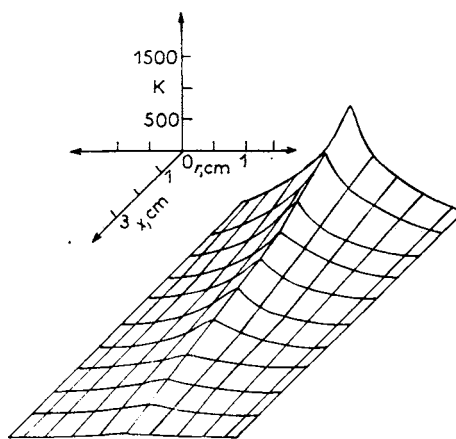


FIG. 1

Temperature distribution ($T_{\max} = 1950$ K) computed for the reactant-SF₆-argon system exposed to *cw* CO₂ laser radiation (4 W output, effective beam radius 0.8 mm, partial pressure of sensitizer 1.4 kPa, wall temperature 300 K, thermal conductivity *K* assumed to obey relation $K = K_{300} \cdot (T/300)^m$)

RESULTS AND DISCUSSION

Chemical reactions induced with a cw CO₂ laser and sensitized with SF₆ have a non-uniform temperature distribution that can be, neglecting convection, computed from the steady state heat conduction equation¹¹. The temperature distribution for the reaction conditions under those the LPHP of bromoethane and 1-bromopropane was studied is illustrated in Fig. 1. The temperatures seen ($T_{\max} = 1\,950\text{ K}$) are lower than those obtained *via* the same procedure for the conditions relating to the LPHP of chlorinated hydrocarbons⁸ ($T_{\max} = 2\,400\text{ K}$), despite that the mean effective temperatures calculated for the dehydrobromination of bromoethane and 1-bromopropane (Table I), and the dehydrochlorination of chlorinated hydrocarbons⁸

TABLE I

Mean effective temperature, T_{eff} , and rate constant, k , with the laser-powered homogeneous dehydrobromination of bromoethane and 1-bromopropane

Reactant	$T_{\text{eff}}^a, \text{K}$	$10^2 \cdot k^b, \text{s}^{-1}$		
		A	B	C
Bromoethane	745—796	1.69	1.36	1.51
1-Bromopropane	748—756	1.36	1.36	1.52

^a Defined⁶ as $E_A/2.3R(\log A - \log k)$, where k is the experimentally found first-order rate constant of the laser-driven dehydrobromination, E_A and A are the Arrhenius parameters for the conventional dehydrobromination under maximum inhibition with alkenes taken from ref.¹. ^b Total rate constant (Eq. (1)) of the dehydrobromination in the reactant-SF₆-argon system (A), the system with propene (B), and the system with chloroethane (C); relative error lower than 6 percent.

TABLE II

First-order rate constant, k , for the laser-induced dehydrochlorination of chloroethane in the presence of bromoethane and 1-bromopropane^a

Admixture	$10^3 \cdot k, \text{s}^{-1}$
—	4.07
Bromoethane	4.08
1-Bromopropane	4.31

^a In chloroethane-SF₆-argon system, Eq. (1), relative error lower than 6%.

are comparable. This disagreement can be brought about by a lower activation energy of the laser-induced dehydrobromination compared to that for the conventional reaction (213–225 kJ mol⁻¹, ref.¹) taken for the calculation of the effective temperature. Such an explanation is in harmony with the findings that the technique of the shock-tube pyrolysis eliminating heterogeneous effects similarly as the LPHP yields¹² the activation energy of dehydrobromination of bromoethane only 130 kJ mol⁻¹.

As a probe for the reaction mechanism of the laser-induced dehydrobromination both the effect of the addition of propene retarding the radical-chain process and that of chloroethane the dehydrochlorination of that is sensitized with radical-chain decomposition of bromoethane in the absence of cyclohexene upon the reaction course was examined. Both the admixtures to the bromoalkane-SF₆-argon system can be considered¹⁰ not to influence the temperature distribution so as the comparison of the cw CO₂ laser photosensitized (SF₆) dehydrobromination of bromoethane and 1-bromopropane with or without the probing agents can be made.

The LPH of bromoethane and 1-bromopropane progresses in the absence or in the presence of propene in the same way and no induction period is indicated. The absence of the induction period and no effect of propene can be attributed to a molecular mechanism of the laser-induced dehydrobromination. Such a view is in harmony with the observation that the rate of the laser-induced dehydrochlorination of chloroethane in the presence of bromoethane (Table II) is not enhanced compared to the same reaction in the absence of the latter compound, because the conventional dehydrochlorination of chloroethane is sensitized in the absence of radical-chain inhibitor by radical chain decomposing bromoethane, but not affected in the presence of radical-chain inhibitor when bromoethane decomposes by a molecular reaction². The molecular mechanism of the laser-induced dehydrobromination is also approved by the absence of the products of the radical-chain process (ethane and bromoethane).

The results thus seem to point out that similarly to the laser-induced dehydrochlorination of some chlorinated hydrocarbons⁸ also the gas-phase radical-chain mechanism of the dehydrobromination of bromoethane and 1-bromopropane can be suppressed by avoiding hot surface effects and can be considered as a molecular reaction when CO₂ laser is taken as a tool for the reaction inducement.

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