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LASER-POWERED HOMOGENEOUS DECOMPOSITION OF 1-BROMO-1-CHLORO-2,2,2-TRIFLUOROETHANE

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SUMMARY

CW CO_2 photosensitized (SF_6) homogeneous decomposition of 1-bromo-1-chloro-2,2,2-trifluoroethane yields various halobutenes and haloethanes. The former are suggested to arise from a sequence of C-Br cleavage, radical recombinations to halobutanes and consecutive β-elimination of hydrogen halides, while the latter appear to be produced by radical recombination or radical H abstraction reactions.

INTRODUCTION

1-Bromo-1-chloro-2,2,2-trifluoroethane (halothane, BCTFE) has been widely used as an anesthetic and its photo- and radiation induced chemistry has been studied to elucidate possible toxic intermediates in its metabolism [1-3]. Data on thermal behavior are not complete [4-6], despite the fact that such knowledge becomes increasingly important for the safe handling of BCTFE in anesthesiology and because of the potential use of BCTFE as a working medium for hydrogen halide lasers as well as working substance for laser-induced separation of hydrogen isotopes. The conventional thermal decomposition of BCTFE can be surface--assisted, since it was observed [5] that it is accelerated in the presence of iron.

Continuous-wave CO_2 laser photosensitized reactions of some fluorinated compounds differ [7-9] from those carried out as conventional thermally-induced reactions, the reason being the absence of hot wall effects. This paper reports CO_2 laser powered decomposition of BCTFE and shows its truly homogeneous course. The decomposition is carried out in the presence of stable sulfur hexafluoride that absorbs laser radiation and acts as energy conveying agent [10].

EXPERIMENTAL

Continuous-wave (cw) CO_2 laser-photosensitized (SF_6) decomposition was carried out by irradiation of BCTFE (72 mbar) - SF_6 (21 mbar) and BCTFE (10 mbar) - SF_6 (24 mbar) - 2-butene (60 mbar) mixtures in a stainless steel tube (10 cm x 3.6 cm I.D.) reactor furnished with two NaCl windows, a sleeve with rubber septum and a valve through which the reactor was connected to a standard vacuum-line. The cw CO_2 laser was operated at the P(20) line of the $00^{0}1 \rightarrow 10^{0}0$ transition (944 19 cm^{-1}) and its beam was focussed with a Ge lens (10 cm focal length) into the middle of the reactor The mixtures were irradiated for measured periods of time and checked for their IR spectrum Thereafter, helium was expanded into the reactor and samples of the gaseous mixture were withdrawn through the septum by a syringe and injected into the mass spectrometer The analyses were performed on a gas chromatograph-mass spectrometer (GC-MS) (GCMS Shimadzu, Model Q P 1000) The progress of the decomposition was estimated by using the sensitizing SF_6 as an internal standard

CW CO_2 photosensitized decomposition of 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane (DCHFB) was performed similarly with mixture DCHFB (73 mbar) - SF_6 (20 mbar)

The effective mean temperature [10] of the BCTFE decomposition was estimated from the rate of the cw CO_2 laser-powered decomposition of ethyl acetate (EA) in the mixture EA (72 mbar) - SF_6 (21 mbar) using the same irradiation conditions as with BCTFE The decomposition progress was monitored by using a Specord model 75 i r spectrometer at 1385 cm^{-1} The effective temperature was calculated using the Arrhenius parameters for EA decomposition taken from ref [11]

Mass spectra were interpreted consulting ref [12] and known abundance ratios for chlorine and bromine isotopes

SF_6 (Fluka) was the commercial sample and DCHFB was obtained as a by-product of the UV-induced addition of BCTFE to chlorotrifluoroethylene [13]

RESULTS AND DISCUSSION

CW CO_2 laser-photosensitized (SF_6, 8 W laser output) decomposition of BCTFE affords (Fig 1)* a mixture of halobutenes $CF_3CH=CClCF_3$, $CF_3CH=CBrCF_3$, $CF_3CCl=CClCF_3$ and $CF_3CCl=CBrCF_3$ and halogenated ethanes CF_3CH_2Cl, CF_3CHCl_2 and CF_3CClBr_2 Apart from these, also traces of CF_4, $CF_2=CHF$, $CF_2=CFCl$ and $CF_3CH=CHCF_3$ are formed at high conversions Table I shows that the quantities of all the major components, though steadily increasing throughout the decomposition progress, do not achieve limits predicted by their low-conversion values This can be attributed to the participation of the products in polymerization reactions, since a brown solid is permanently deposited on the reactor surface during the irradiation Gas phase estimation of HCl and HBr by IR spectroscopy shows that the former noticeably prevails HF was not detected The reaction threshold appears at the laser output 7 W and the mean effective temperature of the BCTFE decomposition with 8 W laser output reaches 730 K

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* Column, 2 1 m, packed with Porapak S, helium carrier gas flow-rate, 20 ml, programmed temperature 100-240°C Peak identification 1 - SF_6, 2 - $CF_2=CFH$, 3 - CF_4, 4 - $CF_2=CFCl$, 5 - $CF_3CH=CHCF_3$, 6 - CF_3CH_2Cl, 7,8 - $CF_3CH=CClCF_3$ (isomers), 9 - CF_3CHCl_2, 10 - $CF_3CH=CBrCF_3$, 11,12 - $CF_3CCl=CClCF_3$ (isomers), 13 - $CF_3CHBrCl$, 14,15 - $CF_3CCl=CBrCF_3$, 16 - CF_3CClBr_2

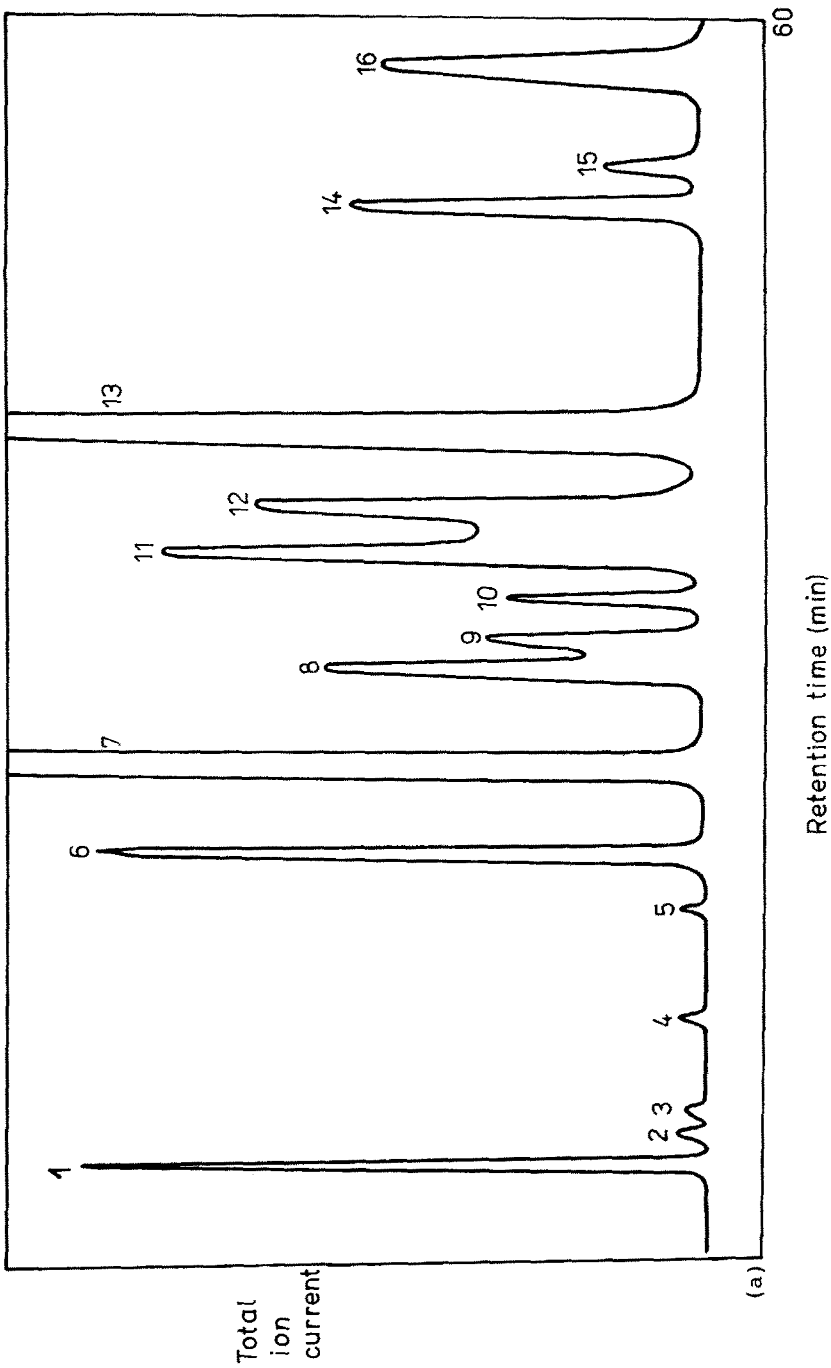
TABLE I

Data on laser-powered decomposition of BCTFE

	TIC* at conversion**			
Product	14 %	49 %	61 %	95 %
$CF_2=CFH$	0	0	0	0 02
CF_4	0	0	0	0 01
$CF_2=CFCl$	0	0	0	0 02
$CF_3CH=CHCF_3$	0	0	0	0 02
CF_3CH_2Cl	0 30	0 35	0 50	0 58
$CF_3CH=CClCF_3$	1 53	2 40	2 60	2 62
CF_3CHCl_2	0 06	0 10	0 10	0 15
$CF_3CH=CBrCF_3$	0 05	0 10	0 10	0 15
$CF_3CCl=CClCF_3$	0 39	0 96	1 35	2 12
$CF_3CCl=CBrCF_3$	0 15	0 20	0 20	0 25
CF_3CClBr_2	0 20	0 50	0 55	0 60

*Total ion current normalized as TIC of product/TIC of SF_6

**Percent of $CF_3CHBrCl$ decomposed, the individual conversions correspond to irradiation time 10, 30, 40 and 100 sec, respectively


Total ion current
Retention time (min)
60
(a)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

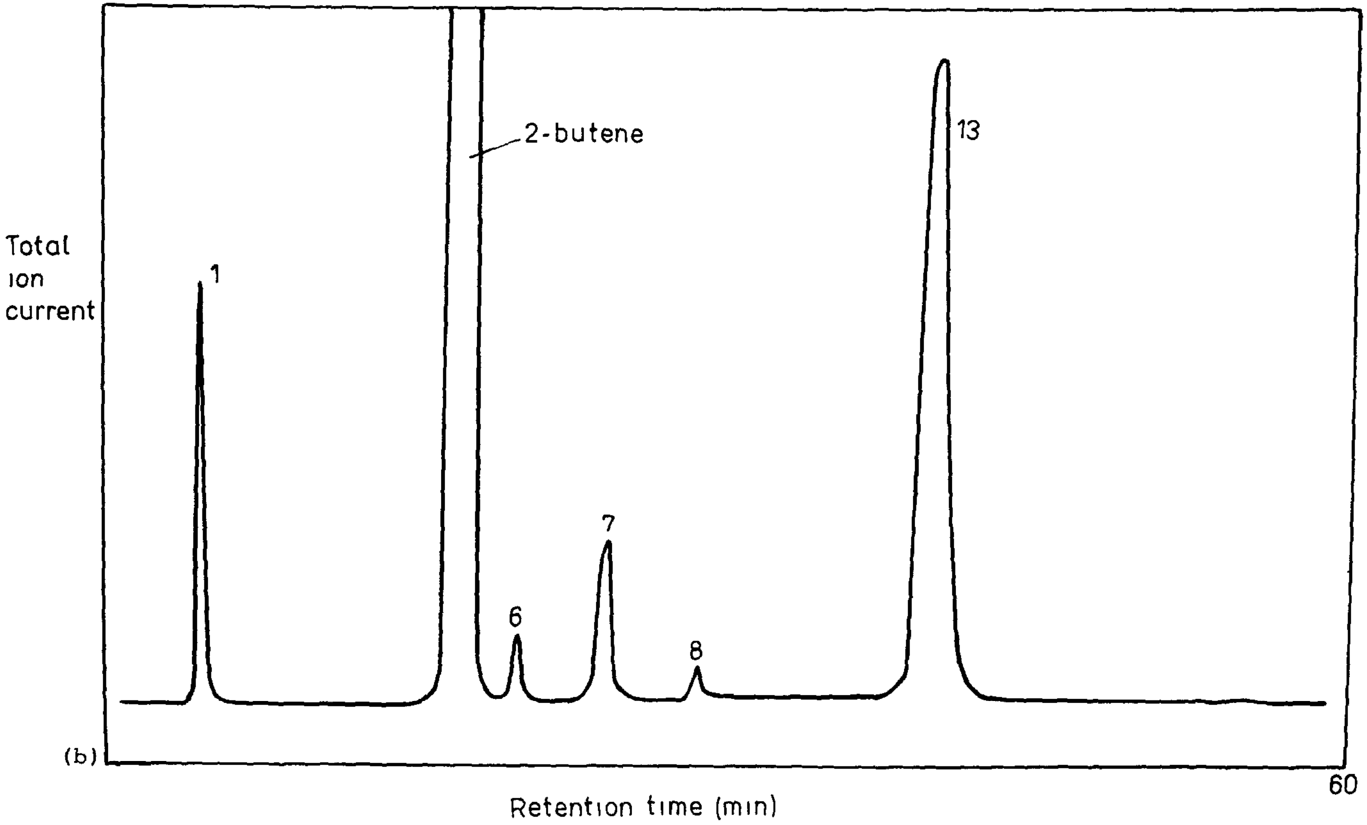


Fig 1 Typical GC-MS traces of the mixture obtained by laser-powdered decomposition of BCTFE driven to high (~90 %) conversion (a) and low conversion (~5 %) in the presence of 2-butene (b)

The reaction conditions used are very similar to those (130-210 mbar, 693 K) under which the conventional thermal decomposition of BCTFE was studied by Iwasuki *et al* [6], who observed that reaction yields only halobutenes and explained their formation by α-elimination (Scheme 1) and recombinations of carbenes

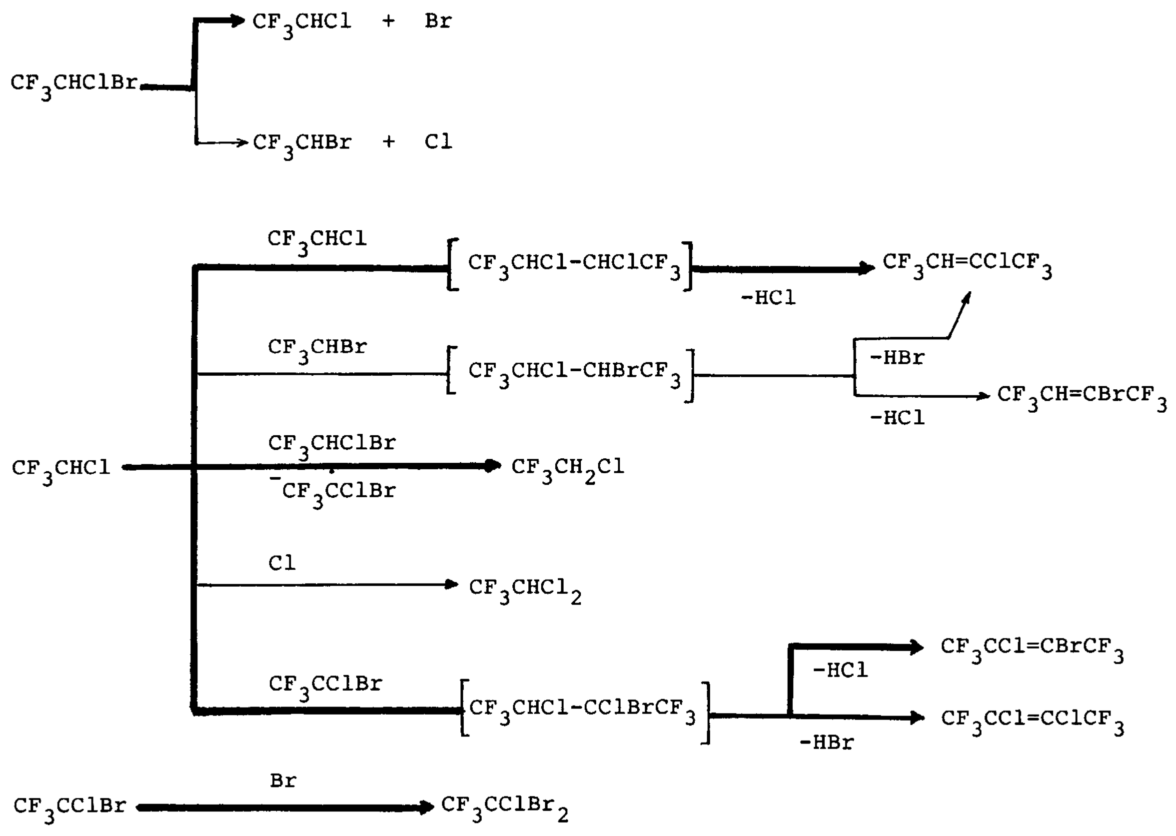
$$\mathrm{CF_3CHBrCl} \longrightarrow \mathrm{CF_3CBr} + \mathrm{HCl}$$

$$\longrightarrow \mathrm{CF_3CCl} + \mathrm{HBr}$$

$$\longrightarrow \mathrm{CF_3CH} + \mathrm{BrCl}$$

Scheme 1

It is, however, conceivable that aside from this carbene mechanism halobutenes can be formed by a sequence of the C-Br (or C-Cl) bond cleavage, the recombination of radicals and β-elimination of hydrogen halide from the products of the radical recombination (Scheme 2) Halogenated ethanes accompanying the halobutenes in the laser-driven process strongly suggest this radical mechanism that was anticipated by Larsen [14] on the basis of results of Scipioni *et al* [5] who examined the thermal decomposition of BCTFE at 773 K The initial cleavage of the weak C-Br bond is supported by mass spectral fragmentation of BCTFE (20 eV, m/z, relative intensity) 196 (M, 34), 177 (M-F, 5), 127 (M-CF_3, 15), 117 (M-Br, 100), 98 (CF_3H, 7), 69 (CF_3,


CF3CHClBr
CF3CHCl + Br
CF3CHBr + Cl
CF3CHCl
CF3CHCl
[CF3CHCl-CHClCF3]
-HCl
CF3CH=CClCF3
CF3CHBr
[CF3CHCl-CHBrCF3]
-HBr
-HCl
CF3CH=CBrCF3
CF3CHClBr
-CF3CClBr
CF3CH2Cl
Cl
CF3CHCl2
CF3CClBr
[CF3CHCl-CClBrCF3]
-HCl
-HBr
CF3CCl=CBrCF3
CF3CCl=CClCF3
CF3CClBr
Br
CF3CClBr2

Scheme 2

9) and 67 (CFHCl, 21). Although none of the halobutanes was detected, it is safe to presume that their dehydrohalogenations are fast enough to annihilate these intermediary species. Thus, it was observed that while DCHFB decomposition into $CF_3CH{=}CClCF_3$ is completed during 10 s irradiation, that of BCTFE proceeds to only 15 % conversion. Both BCTFE and DCFHB do not have absorption bands between 900-1000 cm^{-1} and their decomposition can occur only via collisions with energized sulfur hexafluoride. Further evidence against the carbene mechanism is provided by laser-powered decomposition of BCTFE in excess of 2-butene. It is known [15,16] that singlet fluorocarbenes add across the double bond of olefins. No products of such reaction were, however, detected and the occurrence of only CF_3CH_2Cl and $CF_3CH{=}CClCF_3$ compounds as decomposition products (Fig. 1b) supports the Scheme 2 and shows that important reaction steps taking place during the absence of 2-butene (designated by thick arrows) dominate the BCTFE decomposition also in the presence of the olefin.

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