CW CO$_2$ LASER-INDUCED HALOGEN EXCHANGE REACTION BETWEEN HEXAFLUOROBENZENE AND BORON TRICHLORIDE*

Pavel Engst[a], Milan Horák[a] and Josef Pola[b]

[a] *Institute of Physical Chemistry and Electrochemistry,*
Czechoslovak Academy of Sciences, 118 40 Prague 1 and
[b] *Institute of Chemical Process Fundamentals,*
Czechoslovak Academy of Sciences, 165 02 Prague - Suchdol

The halogen exchange reaction between hexafluorobenzene (HFB) and boron trichloride, BCl$_3$ initiated by a continous-wave CO$_2$ laser primarily affords chloropentafluorobenzene, C$_6$F$_5$Cl and dichlorofluoroborane, BCl$_2$F. For the reaction initiation a number of rotational-vibrational lines of the vibrational 00°1→10°0 transition was used. With wavenumber radiation 977·21 cm^{-1} a faster V—V energy transfer between HFB and BCl$_3$ molecules may occur. For this case the rate of the exchange reaction was observed to be by an order of magnitude higher compared to the reaction initiated by the laser radiation at 949·48 cm^{-1} and carried out under the identical absorption conditions.

First studies on the initiation of chemical reactions by the infrared CO$_2$ laser radiation were issued about ten years ago[1-3]. Since then many reactions of this type were scrutinized and classified[4,5], most common of those are monomolecular decompositions and isomerizations. For the reaction initiation both continuous-wave and pulsed lasers were used. Some reactions were initiated in the presence of sensitizers as SF$_6$ or BCl$_3$, the compounds that absorb strongly energy of laser radiation and transfer it subsequently to reactant molecules.

This paper presents a study of the *cw* CO$_2$ laser-initiated reaction between hexafluorobenzene and boron trichloride that did not behave under used conditions as a sensitizer but underwent an exchange reaction with hexafluorobenzene.

EXPERIMENTAL

A *cw* CO$_2$ laser with about 20 W output on each rotational-vibrational line constructed in our laboratory was used for the irradiation. The lines were selected by diffraction grating (81 grooves per mm) and the output power obtained by means of semitransparent mirror (85% reflection) was measured using a Coherent Model 201 power meter.

---

* Partly presented at the EKON-80 Conference (Conference on Quantum Electronics and Nonlinear Optics), Poznan, April 1980.

The reactions were performed in glass tube-like cells which were 9·5 cm long and had an internal diameter of 4·5 and 2·6 cm with NaCl or KBr windows cemented with Araldit (Ciba, Geigy) that reacted neither with reactants nor with reaction products. Perfluorinated kerosene served as a vacuum grease, the vacuum valves were equipped with P.T.F.E. insertions. While the exchange HFB–BCl_3 reaction was initiated by an unfocussed laser beam, in the absence of BCl_3 the focussed irradiation (Ge lens with focal length 25 cm) had to be used in order to carry out decomposition of HFB.

Commercial samples of boron trichloride (Matheson) and hexafluorobenzene (Imperial Smelting) were used without further purification. Chloropentafluorobenzene was prepared by a treatment of hexafluorobenzene with sulfuryl chloride[6].

A Perkin–Elmer Model 621 infrared spectrometer was used to analyze and identify reaction products and to analyze the concentration of reactants and C_6H_5Cl ($\varepsilon_{max} = 1·103$ kPa^{-1} cm^{-1} for the center of the absorption band at 884 cm^{-1}). The partial pressures were settled by means of a manometer first and checked thereafter from the IR spectra of the reaction sample — the experimental error varies in the range of $\pm 0·03$ kPa.

RESULTS

The CO_2 laser radiation is absorbed by gaseous HFB due to HFB rotational-vibrational band centered at 1 011 cm^{-1}. During the irradiation of gaseous HFB (2·7 kPa) by the R(22) line of the $00°1 \rightarrow 10°0$ transmisison (977·21 cm^{-1}) with 16 W output 20% of the energy was absorbed, this amount being sufficient to initiate HFB decomposition. This decomposition was indicated by clearly orange fluorescence in the hot absorption zone. The absorption of laser radiation by the sample does not practically alter in the course of the decomposition, this apparently indicating that both HFB and the products of the decomposition absorb the R(22) radiation equally well. However, the diminishing extent of the fluorescence was observed with decomposition progress.

The major product of the HFB decomposition is perfluorotoluene, identified from the comparison of the IR spectra of the reaction mixture and that taken from literature[7]. Along with other unidentified compounds, tetrafluoromethane (absorption band at 1 282 cm^{-1}, v_3), hexafluoroethane (absorption bands at 1 251, 1 117, and 714 cm^{-1}, v_{10}, v_5, and v_6, resp.) and tetrafluoroethylene (absorption bands at 1 337 and 1 186 cm^{-1}, v_9 and v_{11}, resp.) are formed in small quantities during the decomposition as well.

The decomposition of HBF can be also induced when gaseous mixture of HFB and SF_6 is irradiated by P(30) line of the $00°1 \rightarrow 10°0$ transmission (934·9 cm^{-1}) with 21 W output. Under these conditions SF_6 acts as the only absorber and also as the sensitizer of the laser radiation. Both different decomposition of HFB, i.e. the one due to the absorption of HFB and that due to the absorption of SF_6, occur in an analogous fashion and afford the products yielded also by a conventional thermal HFB decomposition.[8]

A dissimilar behavior of HFB is observed when this compound is irradiated

in a mixture with BCl_3, when no products of HFB pyrolysis are formed and the reaction initated by the CO_2 laser leads to the exchange of the halogens between HFB and BCl_3. (Similar exchange reaction takes place at high temperatures between HFB and sulfuryl chloride[6].)

Hexafluorobenzene can exchange one or more fluorine atoms for chlorines, the first reaction step being described as the reaction (A).

$$C_6F_6 + BCl_3 \rightarrow C_6F_5Cl + BFCl_2 \qquad (A)$$
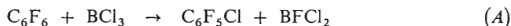
Due to a negligent decrease in quantities of absorbing molecules of reactants no significant change in absorption of the laser radiation occurs after 5 s from the reaction inducement; a great variation in absorption of the laser radiation would, certainly, have a more noticed impact on the reaction course. The compounds of the type $C_6F_nCl_{5-n}$ with $n > 1$ weie observed to arise in negligent amounts only after prolonged irradiation, their formation being influenced with experimental conditions.

One of the products of the exchange reaction, $BFCl_2$, undergoes under the conditions used fast disproportionation (Eq. (B)).

$$2\,BFCl_2 \rightarrow BCl_3 + BF_2Cl \qquad (B)$$
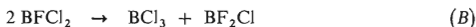
Similar disproportionation takes place also with BF_2Cl, the reaction giving $BFCl_2$ and BF_3, and the reaction mixture can then be described by equilibria between all four boron halogenides BF_nCl_{3-n}. The occurrence of the individual boron halogenides is related to their F/Cl ratio[9]. For the identification of these boron compounds and the estimation of their relative amounts their IR spectra[10] proved to be very helpful.

Fig. 1 shows the concentration variation of reactants and products during the first reaction stage (Eq. (A)). The data on amounts of individual compounds are
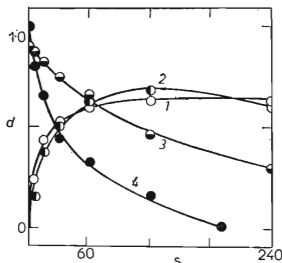
FIG. 1

The plot of the extinction of the analytical absorption bands of reactants (BCl_3 3 and HFB 4) and reaction products (C_6H_5Cl 2 and $BFCl_2$ 1) vs time for the exchange reaction (A)

substituted by values of extinction of their analytical absorption bands. As the reaction progresses, the amounts of reactants decrease and concentration variations of reaction products follow the more complicated pattern. Thus, the concentration of C_6F_5Cl increases at first and then decreases in consequence of the continuing exchange of F and Cl atoms.

The results of the study of the reaction under different experimental conditions are gathered in tables. Table I gives data from experiments wherein different lines of CO_2 laser radiation were used for the sample excitation, and reflect the reaction dependence upon the laser output and the pressure ratio of the reactants. Table II compiles results obtained from the experiments in which the effect of inert gas, xenon, was studied and Table III presents the experiments pumped by the CO_2 laser lines coinciding with the HFB absorption band.

DISCUSSION

The analysis of the reaction mixture arising from the irradiation of gaseous HFB and BCl_3 compounds by cw CO_2 laser can be used to explain the chemistry of the laser-induced process rather well. An interpretation of the reaction as for the mechan-

TABLE I

The exchange reaction between BCl_3 and HFB using the excitation of $^{11}BCl_3$

Run No	Reactants[a]		Laser Line			Yield		Reaction rate[d]
	p_{BCl_3}	p_{HFB}	No	wavenumber, cm^{-1}	power, W	%[b]	quantum[c] . 10^5	Pa s^{-1}
1	2·53	0·29	P(12)	951·2	15	70	0·10	6·54
2	3·01	0·35	P(14)	949·5	15	62	0·30	15·78
3	2·78	0·47	P(16)	947·7	15	76	0·17	17·43
4	2·85	0·31	P(18)	946·0	15	72	0·03	3·04
5	2·50	0·45	P(20)	944·2	15	74	0·16	14·73
6	2·65	0·43	P(22)	942·4	15	73	0·05	11·05
7	2·69	0·31	P(24)	940·6	15	62	0·04	14·95
8	2·65	0·43	P(14)	949·5	12	77	0·06	2·63
9	2·22	0·36	P(14)	949·5	19·5	48	0·71	29·30
10	3·33	0·89	P(14)	949·5	13·5	37	2·44	66·12
11	3·51	3·36	P(14)	949·5	13·5	60	0·06	60·49
12	0·80	2·89	P(14)	949·5	18·5	52	0·03	1·01
13	4·26	0·29	P(14)	949·5	14	27	1·96	42·53

[a] Pressure (in kPa) in the cell before irradiation; [b] pressure ratio C_6F_5Cl formed: C_6F_6 reacted; [c] number of reacted molecules per photon absorbed; [d] Initial rate of exchange reaction.

ism of the energy transfer poses, however, a more difficult problem considering that the known data at our disposal are only the initial reaction rate, quantum yield (the number of molecules reacted per one photon absorbed), the amount of C_6F_5Cl formed relative to the initial amount of HFB and to the amount of HFB reacted.

The laser-initiated reaction is preceded by a pumping process. The CO_2 laser lines at $940 \, cm^{-1}$ were mostly made use for the reaction initiation, for these lines coincide with ν_3 absorption band of $^{11}BCl_3$ compound, while HFB is only a very

TABLE II

The effect of inert gas, xenon on the BCl_3–HFB exchange reaction initiated *via* $^{11}BCl_3$

Run No	Components[a]			Laser line			Yield[b] %	Reaction rate[c] Pa s^{-1}	∅[d] mm
	p_{BCl_3}	p_{HFB}	p_{Xe}	No	wavenumber cm^{-1}	power, W			
14	2·5	0·45	—	P(20)	944·2	15	76	14·73	40
15	2·7	0·56	5·3	P(20)	944·2	15	48	60·11	40
16	2·6	1·02	—	P(14)	949·5	18·5	57	20·29	40
17	2·0	0·68	15·3	P(14)	949·5	18·5	60	6·39	40
18	2·5	1·73	—	P(22)	942·4	18·5	42	172·82	26
19	2·9	1·42	6·7	P(22)	942·4	18·5	34	270·50	26
20	1·8	1·30	5·3	P(20)	944·2	20	93	[e]	40

[a] Pressure (in kPa) before irradiation; [b] pressure ratio C_6F_5Cl formed: C_6F_6 reacted; [c] initial rate of exchange reaction; [d] cell diameter; [e] not determined.

TABLE III

The exchange reaction between BCl_3 and HFB using excitation of $^{10}BCl_3$ and HFB

Run No	Components[a]			Laser line			Yield[b] %	Reaction rate[c] Pa s^{-1}
	p_{BCl_3}	p_{HFB}	p_{Xe}	No	wavenumber cm^{-1}	power, W[d]		
21	0·4	2·7	—	R(22)	977·2	18 (14·8)	67	14·28
22	0·3	2·1	5·3	R(22)	977·2	16·5 (11·7)	67	27·05
23	2·7	1·5	—	R(24)	978·5	19 (19)	44	32·31

[a] Pressure (in kPa) before irradiation; [b] pressure ratio C_6H_5Cl formed: C_6F_6 reacted; [c] initial rate of the exchange reaction; [d] in parentheses the power absorbed.

weak absorber in this region (Fig. 2). The pumping process can thus be envisaged as a one photon absorption of the radiation by $^{11}BCl_3$ molecules which is responsible for the increase in vibrational temperature of gaseous mixture inside the absorption zone. This process is ensued by relaxation phenomena by which the vibrational energy of excited molecules is transformed into other energy forms. Intermolecular collisions of the excited BCl_3 molecules make relatively fast $V-V$ energy transfer possible and lead thus to population of high vibrational levels[11]. Higher vibrational levels of HFB molecules may be populated by collisions of vibrationally excited BCl_3 molecules with HFB molecules as well. These processes compete with the energy transfer $(V-T, V-R$ and $R-T)$ processes by means of those the energy absorbed is thermalized. The reactions initiated bear almost always the threshold behavior[12]. Assuming that the higher vibrational level achieved by the laser excitation, the higher probability of a molecule to overcome Arrhenius energy barrier of reaction, we feel that process (A) is better to describe by Eq. (A').

$$C_6F_6^{n*} + BCl_3^{m*} \rightarrow C_6F_5Cl + BFCl_2 + \Delta E_T \qquad (A')$$

where asterisk designates vibrational excitation and coefficients n and m relate to appropriate vibrational levels.

The rate of the reaction (A') depends on the concentration of the reactants (Table I). The increase of the pressure of the absorbing compound (runs 2 and 13) results in an almost exponential rate increase, while the increasing of the pressure of HFB induces a rate increase of rather a linear character. This statement is, however, of a limited validity. Thus for the pressure of HFB higher than that of BCl_3 there operates rather a "cooling" effect of HFB which brings about a steep decrease of reaction rate (Table I, run 12).

An increase in the laser output causes a significant increase of the reaction rate (Fig. 3) and simultaneously leads to an increase of quantum yields (Table I, runs 2, 8 and 9). The laser output being higher, all the stages of the exchange reaction become faster, which lead to a greater occurrence of polychloropolyfluorosubstituted benzenes. This effect results in a decrease of the ratio C_6F_5Cl formed: HFB reacted in the first reaction stage. The effect of the variation of the pumping frequency (by one rotational-vibrational line) upon the reaction course is relatively small (Table I, runs $1-7$). The variation of the reaction rate and of the yield of C_6F_5Cl is most likely due to small differences in absorption of BCl_3 observed for the individual pumping lines (Fig. 2), and might be also the consequence of unequal pressures of the reactants in the individual runs.

The reaction rate also experiences the effect of the addition of inert gas (xenon). The experiments show two mechanisms of its action. The addition of little amounts of xenon (5 kPa, Table II, run 15) reflects probably the fact that reactants molecules

undergo on their way from the hot absorption zone collisions with heavy molecules of xenon and are forced to return to the hot zone. This results in an increase in the exchange reaction rate. The addition of a greater amount of xenon (15 kPa, Table II, run 17) may decrease the number of effective collisions between the reactants inside the hot zone and leads to a decrease of the reaction rate.

A profound increase in the reaction rate was found in experiments with a reactor of a smaller diameter (Table II, run 18 and 19). In order to explain this fact, knowledge of the process dynamics is necessary. Studies on the laser irradiation of SF_6^{13} have shown that cw CO_2 laser brings about convection: hot gas species assend from the hot absorption zone and initiate a circulation of gases in the cell. The hot absorption zone during the reaction betwen HFB and BCl_3 is directly observable as intensive fluorescence apparently arising from excited reaction intermediate species. The zone represents only about 4 percent of the total cell volume. The decrease of the diameter of the cell diminishes energy losses by heat conduction through the cell walls and all other conditions being held constant, it promotes the circulation effect, and therefore the reaction rate. It thus turns out that a variation of the cell geometry has a pronounced effect upon the course of the CO_2 laser-initiated reaction.

Up to now only those experiments were dealt with wherein the laser radiation was totally absorbed in the HFB/BCl_3 mixtures. Depending on the experimental
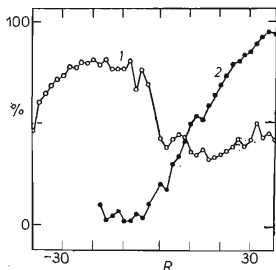

FIG. 2

The absorption (A) of the P and R lines of the laser radiation (00°l→10°0 transmittion) in gaseous BCl_3 (1 0·53 kPa) and HFB (2, 2·66 kPa) with optical path length 9·5 cm
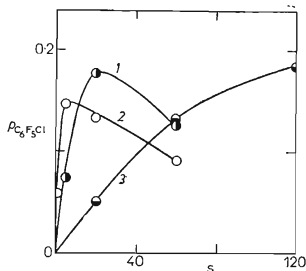
FIG. 3

Formation of C_6F_5Cl ($p_{C_6F_5Cl}$ in kPa) *vs* time in the exchange reaction (A) for different laser outputs. The P(14) line and the output 12 W 3, 15 W 1, and 19·5 W 2 were used. The curves relate to runs 8, 12 and 9 in this order

conditions the hot zone can be variously shaped and have a very different size[13]. Thus, *e.g.* an increase in the laser output, the pressure of absorbing gas remaining constant, results in an increase in the size of the hot zone. Contrary to it an increase of the pressure of the absorbing gas, the laser output being constant, leads to the diminishing of its size. Regarding a great importance of the dynamics of the process, these experiments are therefore hardly to compare.

The above reasons stimulated experiments during which the laser energy is partly transmitted through the cell; these experiments presumably provide similar shape and properties of the hot zone. The mixture HFB/BCl_3 was irradiated by the R(22) line of the $00^\circ 1 \rightarrow 10^\circ 0$ transition (977·21 cm^{-1}) that is absorbed by $^{10}BCl_3$ and HFB molecules. When a mixture of BCl_3 (0·4 kPa) and HFB (2·7 kPa) is irradiated by this line with 18W output 18 percent of the radiation is transmitted through the cell at the early stage of the reaction. The initial reaction rate of the Cl—F exchange reaction is in this case 14·3 Pa s^{-1}. The same amount of laser energy is transmitted also with the P(34) line when the cell is filled with 0·64 kPa of BCl_3. In this case (Table III, run 21; Table I, run 12) the initial rate of the exchange reaction equals to only 1 Pa s^{-1}.

Provided that the above experiments are dominated by V−T energy transfer, the reaction rate in both cases should be comparable. Noticeably higher rate with the R(22) line can be attributed to a high vibrational temperature of molecules in the gaseous mixture. During the irradiation the vibrational excitation of both $^{10}BCl_3$ and HFB molecules is possible due to their absorption of the laser radiation. Additionally, absorption bands of both compounds are very close to each other (the centers of the bands are separated by only 16 cm^{-1}), which may facilitate even an effective V−V energy transfer from $^{10}BCl_3$ molecules to molecules of HFB and *vice versa*. The irradiation by the P(14) line (949·48 cm^{-1}) leads to the excitation of only $^{11}BCl_3$ molecules. Vibrational frequency of $^{11}BCl_3$ and HFB molecules differ more (the centers of the absorption bands are 56 cm^{-1} apart from one another) and the collisional V−V energy transfer between these molecules is non-resonant. Hence, vibrational temperature even in this, *cw* CO_2 laser induced reaction is an important factor even though its operation is not so clear as in the case of chemical reactions initiated by a pulsed CO_2 laser.

The reaction initiated with the R(22) line should respond to the relatively small energy density deposited to the chemical system — this factor should favor the formation of a great amount of C_6F_5Cl. The results are, however, in a disagreement with such an expectation. The molecules of C_6F_5Cl, strongly absorbing radiation at 986 cm^{-1} undergo subsequent F—Cl exchange reaction.

The mechanism of the reaction between HFB and BCl_3, the reaction initiated by $^{11}BCl_3$ or $^{10}BCl_3$ molecules, appears to be consonant with the possibility of a separation of the boron isotopes. This phenomenon is apparently deteriorated by collisional processes and disproportionation reaction (*B*).

The authors appreciate critical reviewing of the contribution by Prof. D. Papoušek and Dr Š. Urban.

REFERENCES

1. Bordé C., Henry A., Henry L.: C. R. Acad. Sci., Ser. B *262*, 1389 (1966).
2. Quel E., DeHemptine X.: Ann. Soc. Sci. Bruxelles *83*, 262 (1969).
3. Basov N. G., Markin E. P., Oreavskii A. N., Pankratov A. V.: Dokl. Akad. Nauk SSSR *198*, 1043 (1971).
4. Grunwald E., Dever D. F., Keehn P. M.: *Megawatt Infrared Laser Chemistry*. Wiley, New York 1978.
5. Steinfeld J. I., Ed.: *Laser Induced Chemical Processes*. Plenum Press, New York 1981.
6. Antonucci J. M., Wall L. A.: J. Res. Nat. Bur. Stand. *70A*, 473 (1966).
7. *Sadtler Standard Spectra*. The Sadtler Research Laboratories, Philadelphia, U.S.A.
8. Desirant Y.: Bull. Soc. Chim. Belg. *67*, 676 (1958).
9. Riley C., Maclean L.: J. Amer. Chem. Soc. *102*, 5108 (1980).
10. *Gmelin Handbuch der Anorganischen Chemie*, 8th Ed., Vol. 53, Part 19, *Borverbindungen* p. 237.
11. Basov N. G., Oraevskii A. N., Pankratov A. V.: Kvant. Elektron. *3*, 814 (1976).
12. Gordiec B. F., Osipov A. I., Shelepin L. A.: *Kineticheskie Procesy v Gazach i Molekularnye Lasery*. Nauka, Moscow 1980.
13. Engst P., Horák M.: Unpublished results.