A COMPARATIVE STUDY OF THE SF_6-SENSITIZED INTERACTION OF A *CW*-CO_2 LASER RADIATION WITH METHYLTRICHLORO DERIVATIVES OF CARBON, SILICON AND GERMANIUM*

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A comparative study of the gas-phase interaction of methyltrichloro derivatives of carbon,silicon and germanium (CH_3MCl_3 where M=C, Si and Ge) with sulfur hexafluoride either excited by a *cw*-CO_2 laser radiation or under conventional static pyrolytic conditions is reported. 1,1,1-Trichloroethane and methyltrichlorogermane do not react with SF_6 under laser irradiation and undergo their decomposition leading to the same products as afforded by heating: CH_3CCl_3 yields $Cl_2C{=}CH_2$ and HCl, and CH_3GeCl_3 gives $HGeCl_3$ along with CH_4 and C_2H_2. Mixtures of methyltrichlorosilane and SF_6 afford under the both conditions products of the CH_3SiCl_3 decomposition —CH_4, C_2H_2, HCl and $SiCl_4$ and products of the CH_3SiCl_3—SF_6 reaction —SiF_4, SCF_2, and CS_2. Possible reasons for the different reactivity of CH_3MCl_3 compounds toward SF_6 are briefly discussed. The decompositions of CH_3GeCl_3 to $HGeCl_3$ offers new way for the preparation of the latter compound.

Despite that sulfur hexafluoride serves as a useful participant in chemical reactions of organic molecules[1], its reactions with organic compounds are very scanty[1,2] and are restricted to very special cases. While the explanation of inability of SF_6 to react with nucleophiles involves no possession of suitable orbitals for coordination with these reagents, the reactions of SF_6 with electrophiles seem more feasible due to possible interaction of electrophiles with SF_6 fluorines' electron pairs[3]. From this point of view the examination of the SF_6 reactivity toward organic compounds differring in their ability to act as electrophiles appears worthy. Methyltrichloro derivatives of carbon, silicon, and germanium appear to be appropriate for the examination of the influence of reagent's electrophilicity upon its reactivity toward SF_6 since the display of a different character of C, Si, and Ge in these compounds is well estab-

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lished[4,5]. Recent discovery of the possibility of decreasing the activation energy of reaction by a specific vibrational excitation of reactants[6-8] and the ability of the CO_2 laser radiation to efficiently achieve high vibrational excitation of SF_6 (ref.[9,10]) support the chance of enhancing the SF_6 reactivity by the new way. By absorption of a *cw*-CO_2 laser radiation SF_6 can acquire a lot of kinetic energy as well. Using this fashion of the SF_6 excitation, we report in this paper the behavior of CH_3MCl_3 compounds (M=C, Si, and Ge) in mixtures with SF_6 irradiated with a cw-CO_2 laser beam and compare it to their thermal decompositions.

EXPERIMENTAL

The irradiation experiments were performed in a cylindrical stainless steel cell (11 cm path length, 2·5 cm i.d.) equipped with one needle valve and two NaCl windows. A *cw*-CO_2 laser[11] operating on the P(34) line of the $00^01 \rightarrow 10^00$ transition (931 cm^{-1}) with output of 10 W was used for the irradiation of gaseous SF_6–CH_3MCl_3 mixtures, the laser beam being focussed with a 25 cm focal length Ge lens either directly at the entrance window or into the middle of the cell.

Pyrolyses of the SF_6–CH_3MCl_3 mixtures and that of methyltrichlorogermane were carried out in a static stainless steel reactor.

Samples for pyrolysis and laser irradiation experiments were prepared by a standard vacuum-line technique. An infrared spectrometer Perkin–Elmer 621 was used to analyse the composition of reaction mixtures at measured intervals. In order to monitor the depletion of CH_3MCl_3 compounds, the absorption bands at 1 383 cm^{-1} (ν_2), 1 271 cm^{-1} (ν_2), and 825 cm^{-1} (ν_9) were employed to follow 1,1,1-trichloroethane, methyltrichlorosilane, and methyltrichlorogermane, respectively. The disappearance of SF_6 was checked by the absorption band at 932 cm^{-1} (ν_3). As far as the reaction products are concerned, 1,1-dichloroethylene (796 cm^{-1}, ν_9), acetylene (730 cm^{-1}, ν_5), methane (1 306 cm^{-1}, ν_4), carbon disulfide (1 535 cm^{-1}, ν_3), trichlorogermane (705 cm^{-1}, ν_4), and tetrachlorosilane (621 cm^{-1}, ν_3), tetrafluorosilane (1 031 cm^{-1}, ν_3), sulfur tetrafluoride (867 cm^{-1}, ν_6), thiocarbonyl fluoride (1 368 cm^{-1}, ν_2) and hydrogen chloride (2 884 cm^{-1}) were analysed by the same way using their characteristic absorption bands at suitable wavelengths. For this purpose the pure samples of all these compounds were measured by IR spectroscopy in order to know appropriate absorption coefficients.

Of the compounds used, 1,1,1-trichloroethane (Loba-Chemie, Wien), 1,1-dichloroethylene (Fluka AG, Buchs), carbon disulfide (Merck, Darmstadt), methane and acetylene (both Spolek pro chemickou a hutní výrobu, Ústí n.L.), and hydrogen chloride (Lachema, Bohumín) were commercial samples. Methyltrichlorosilanes, methyltrichlorogermane, and tetrachlorosilane were from the laboratory stock. Tetrafluorosilane was prepared by the procedure[12] and trichlorogermane was obtained by a treatment[13] of hydrogen chloride with germanium dichloride.

RESULTS AND DISCUSSION

During the SF_6-sensitized interaction of CO_2 laser radiation with CH_3MCl_3 (M=C, Si and Ge) either a reaction between SF_6 and CH_3MCl_3, or the laser-powered homogeneous pyrolysis[16] might occur. In order to differentiate between these two possibilities the behavior of CH_3MCl_3 compounds under elevated temperature is dealt with first. Thereafter, the attention is paid to the SF_6–CH_3MCl_3 mixtures exposed either to heat or to the laser radiation.

1,1,1-*Trichloroethane*

1,1,1-Trichloroethane (TCE) belongs to the family of saturated chlorinated hydrocarbons undergoing[14] thermal decomposition to the corresponding olefin and hydrogen chloride by two homogeneous, molecular and radical chain, mechanisms both of which occur simultaneously. TCE affords[15] 1,1-dichlorethylene (DCE). The first mechanism follows the first order kinetics with rate constant independent of the initial pressure. The second, chain process, involves chlorine atoms and $Cl_3CCH_2^{\cdot}$ radicals, represents about 75% of the total rate in an empty reactor at temperatures from 636 to 707°K, and obeys first order kinetics only over the initial stages of the decomposition due to the partial inhibition of the process by produced DCE.

Conventional pyrolysis of TCE in the presence of SF_6 commenced in the temperature range 600–700°C with samples TCE – SF_6 (both 13·3 kPa) yields the same compounds as the pyrolysis without SF_6 (Eq. (*A*)). Besides DCE and HCl there

$$Cl_3C{-}CH_3 \rightarrow HCl + Cl_2C{=}CH_2 \qquad (A)$$

were found only traces of tetrafluorosilane in the reaction mixture apparently arising from the contact of activated SF_6 with silicon O-ring in the reactor valve. Obviously, SF_6 does not enter into the reaction with TCE. The same conclusion has been reached at for the *cw*-CO_2 laser irradiations of TCE-SF_6 samples (Table I). In these cases only the laser-powered homogeneous pyrolysis of TCE occurs. The TCE and DCE distribution along the irradiation time is shown in Fig. 1. This TCE decomposition

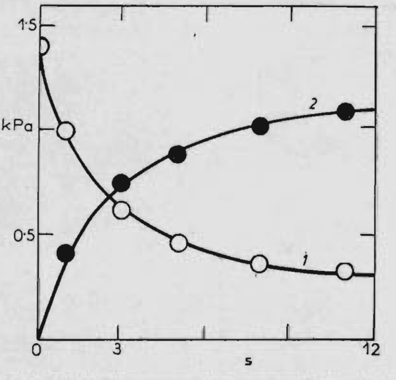

FIG. 1

SF_6-Sensitized interaction of *cw*-CO_2 laser radiation with TCE. The dependence of the mixture composition (*1* TCE; *2* DCE) upon the irradiation time. Run 1 from Table I and as well DCE formation are of the first order in these compounds for the two quite different compositions of the initial TCE–SF_6 mixture. Table I shows that the reaction is facilitated with increasing molar percent of SF_6.

Methyltrichlorosilane

Methyltrichlorosilane (MTS) is the most difficult compound from methylchlorosilanes $(CH_3)_nSiCl_{4-n}$ to undergo thermal redistribution[17,18] of methyl and chlorine substituents at silicon. All these compounds possess reasonable thermal stability since their synthesis has been accomplished[19] at temperatures of 300 to 400°C. The redistribution is accompanied by demethylation that proceeds through the elimination of methane from two methyl groups of silicon and the establishment of a methylene bridge between the silicon atoms. This type of reaction (Eq. (*B*)) is supposed not to be

$$2\,CH_3SiCl_3 \rightarrow CH_4 + Cl_3SiCH_2SiCl_3 \qquad (B)$$

reversible[17]. In minor amounts also interesting caged cyclocarbosilanes arise[20-22], whose production includes elimination of HCl and necessitates temperatures of 700 to 800°C.

Our experiments on the conventional thermal decomposition of MTS in the presence of SF_6 revealed that the mixture of equimolar amounts of both compounds (each 4 kPa) affords at temperatures from 650 to 750°C hydrogen chloride, carbon disulfide, silicon tetrafluoride and minor amounts of thiocarbonyl fluoride. Interestingly, no $SiCl_4$ or $(CH_3)_2SiCl_2$ – the products of redistribution of CH_3 and Cl substituents at the silicon – and no methane or other gaseous hydrocarbons were observed in the mixture. The compounds formed suggest that mainly the elimination of HCl (and not that of CH_4)) takes place. Moreover, SiF_4, CS_2 and SCF_2 can be

TABLE I

Second order rate constant, k_2, of LPHP of TCE sensitized by SF_6

Run[a]	Sample total pressure, kPa	Molar % of SF_6	k_2 $(Pa\ s)^{-1}$
1	2·7	49	4·9
2	2·3	11	2·4

[a] Samples of TCE–SF_6 mixtures were exposed to laser radiation (10 W output) focussed at the entrance window; laser energy was completely absorbed.

considered as the products of a reaction between SF_6 and MTS. Sulfur tetrafluoride was observed to be formed as well. There can be therefore suggested that SF_6 donates sulfur to form CS_2 and is also degraded to SF_4.

The behavior of MTS in the presence of SF_6 under CO_2 laser radiation was studied under different focussing conditions for different MTS–SF_6 composition and different (10–16 W) laser outputs. The variation of the laser output does not affect the products composition and only moderates the decomposition rate. Representative runs including the variation of other parameters are gathered in Table II. With low molar % of SF_6 (run 3) only HCl (traces), CH_4 and also $SiCl_4$ were detected which suggests that mainly the elimination of CH_4 proceeds. No $(CH_3)_2SiCl_2$ was found among the products and the $SiCl_4$ formation *via* the redistribution of CH_3–Si and Si–Cl bonds does not therefore seem probable.

The same products are encountered with when MTS–SF_6 mixture with higher molar % of SF_6 (run 4) is irradiated with laser beam focussed into the middle of the cell. In this case also acetylene is produced.

Equimolar SF_6–MTS mixture and the mixture with a higher SF_6 content (runs 1 and 2) irradiated by the laser beam focussed into the entrance window afford (Fig. 2), along with CH_4, C_2H_2, HCl and $SiCl_4$ also SiF_4 and CS_2. The two last compounds are the products of a reaction between MTS and SF_6 observed also under the conventional pyrolytic conditions.

TABLE II

The SF_6 sensitized interaction of CO_2 laser radiation with MTS

Run[a]	Total pressure of MTS–SF_6 mixture, kPa	Molar % of SF_6	Focussed into	TMS half amount decay time, s	Products, mol per mol of MTS decomposed	Conversion, %
1	2·4	75	entrance window	20	CH_4 (0·30), C_2H_2 (0·22), CS_2 (0·31), HCl, $SiCl_4$, SiF_4	80
2	2·5	50	entrance window	35	CH_4 (0·40), C_2H_2 (0·14), CS_2 (0·15), HCl, $SiCl_4$, SiF_4	80
3	2·0	13	entrance window	$>10^3$	CH_4 (~1·0), HCl (traces), $SiCl_4$	25
4	2·4	52	middle of cell	90	CH_4 (0·62), C_2H_2 (0·19), HCl, $SiCl_4$	80

[a] All runs performed with laser output of 10 W, laser energy was in all events totally absorbed.

It appears (Table II) that the half amount decay time of MTS increases with diminishing SF_6 molar % and when the irradiation is focussed farther inside the cell. The SF_6 content in the initial SF_6-MTS mixture controls 1) the extent of the reaction between MTS and SF_6 (amount of CS_2 produced per amount of TMS decomposed varies from 0 *via* 0·15 to 0·31 when molar % of SF_6 increases from 13 *via* 50 to 75) and 2) the C_2H_2 : CH_4 ratio (this increases with higher SF_6 content (13, 50, and 75%) from 0 *via* 0·35 to 0·73).

Methyltrichlorogermane

To our knowledge there are no data accessible in the literature on the thermal decomposition of methyltrichlorogermane (MTG). As far as the heat-promoted redistribution of Ge–Cl and Ge–CH_3 bonds is concerned, the studies on the equilibration of $GeCl_4$ and tetraalkylgermanes have shown[23,24] that a Lewis-type catalyst is required in order this type of reaction is to proceed and that the transfer of alkyl groups probably occurs *via* alkyl aluminium halides.

Our experiments on the pyrolysis of MTG alone (2·7 kPa), or the MTG–SF_6 mixture (both 2·7 kPa) at 700°C for 15 min show that the only gaseous products are in the both cases HCl, CH_4 and $HGeCl_3$. The first two compounds were disclosed to arise also by the thermal decomposition of MTS. One is therefore tempted to admitt

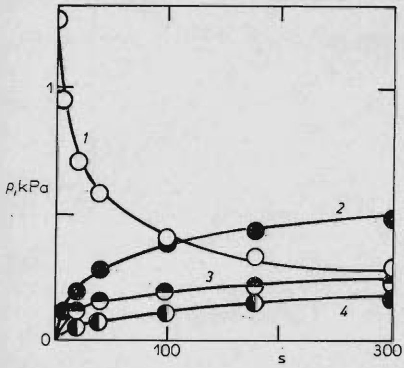

FIG. 2

SF_6-Sensitized interaction of cw-CO_2 laser radiation with MTS. The dependence of the mixture composition (MTS *1*, CH_4 *2*, C_2H_2 *3*, CS_2 *4*) upon the irradiation time. Run 2 from Table II

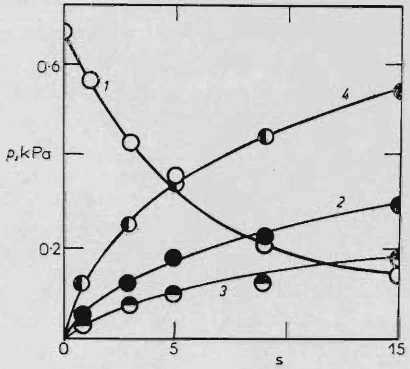

FIG. 3

SF_6-Sensitized interaction of CO_2 laser radiation with MTG. The dependence of the mixture composition (MTG *1*, CH_4 *2*, C_2H_2 *3* and $HGeCl_3$ *4*). Run 1 from Table III that, as in that case, MTG undergoes similar elimination reactions leading possibly to compounds having Ge–CH_2–Ge bridges and/or to caged compounds. Even though the present results do not allow to draw a final conclusion on the exact mechanism of the MTG decomposition and further effort is compulsory, the average bond energies[25,26] of organogermanium compounds suggest that the MTG decomposition is initiated by the homolytic cleavage of the CH_3–Ge bonds and followed by reactions of the CH_3 ·and ·$GeCl_3$ radicals formed with MTG. These reactions should give, along with CH_4 and $HGeCl_3$, also ·CH_2GeCl_3 radical. The formation of HCl probably includes the splitting of the Ge–Cl bond in MTG and simultaneous formation of ·CH_2GeCl_3 radical.

The data on the SF_6 sensitized interaction of cw-CO_2 laser radiation with MTG are given in Table III and show that the only reaction proceeding in the cell is the thermal decomposition of MTG. Apart from CH_4 and $HGeCl_3$ also C_2H_2 is formed whose amount is dependent upon the composition of the initial SF_6–MTG mixture – the $C_2H_2 : CH_4$ ratio increases with higher SF_6 content. Variable amounts of the methane and acetylene detected thus do not permit to understand the MTG decomposition in terms of Eq. (*C*):

$$3\,CH_3GeCl_3 \rightarrow 3\,HGeCl_3 + CH_4 + C_2H_2\,. \qquad (C)$$

We assume that the relative amount of methane and acetylene are controlled by a hot zone temperature, the higher temperature favoring C_2H_2 at the expense of CH_4. The half amount decay time of MTG in runs 1 and 2 are close one to another, this situation not resembling the very different half amount decay time of MTS with correspondingly similar SF_6–CH_3MCl_3 initial compositions. Such a dissimilarity

TABLE III

The SF_6 sensitized interaction of CO_2 laser radiation with MTG

Run[a]	Total pressure of MTG–SF_6 mixture, kPa	Molar % of SF_6	MTG half amount decay time, s	Products mol per mol of MTG decomposed	Conversion, %
1	2·5	73	35	$HGeCl_3$ (1·0), CH_4 (0·50), C_2H_2 (0·25)	80
2	2·0	17	45	$HGeCl_3$ (1·0), CH_4 (0·74), C_2H_2 (0·10)	76

[a] Both runs performed with laser radiation of 10 W output focussed into the entrance window.

is likely associated with the lower energy for homolytic fission of the Ge–C bond ($\sim$58 kJ/mol; Si–C value being $\sim$335 kJ/mol).

A very important feature of the MTG decomposition is, perhaps, to be emphasized now. Trichlorogermane is produced in quantitative yields from methyltrichlorogermane under very simple experimental conditions. The reported[13] preparation of $HGeCl_3$ involves laborious synthesis of germanium dichloride[27] ($Ge + GeCl_4 \rightarrow 2 GeCl_2$) and its following reaction[13] with hydrogen chloride. The thermal decomposition of MTG, especially its laser version offers a new and much less laborious procedure for the preparation of trichlorogermane, the compound so oftenly used in hydrogermylation reactions[28].

CONCLUSION

The decomposition course of methyltrichloro derivatives of silicon and germanium are apparently of a radical nature. The reaction products are in accord with a view that molecular pathway, occurring with 1,1,1-trichloroethane, is much less substantiated with methyltrichlorosilane and methyltrichlorogermane due to very low ability of the Si and Ge atoms to form double M=C bond. The ability of SF_6 to react with CH_3SiCl_3 and not with isostructural carbon and germanium compounds can be attributed to the fact that silicon possesses, contrary to carbon and germanium, highly polarizable vacant orbitals which can be utilized for the unshared electrons of SF_6 fluorine. The reaction between CH_3SiCl_3 and SF_6 is likely initiated by the $Si \leftarrow FSF_5$ coordination interaction. The results herein presented seem to confirm the earlier view[3] that reaction of sulfur hexafluoride can be facilitated especially by pronounced electrophilic character of a reagent.

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