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## REACTIONS OF CHLORODIFLUOROMETHYL RADICALS

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### SUMMARY

The effects of hetero atoms within the substrate molecule and the number of available hydrogen atoms on the hydrogen abstraction reaction are considered. Chlorodifluoromethyl radicals are generated by the photolysis of 1,3-dichlorotetrafluoroacetone and the substrate molecules used are dimethyl ether, trimethylamine and tetramethylsilane. The Arrhenius parameters for the hydrogen abstraction reaction have been calculated and compared with those obtained using other radicals. The role of secondary radical decomposition is considered.

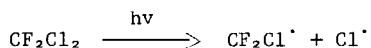
### INTRODUCTION

It has been suggested recently that the continued use of low molecular weight halocarbons as aerosol propellants constitutes an environmental hazard [1]. The halocarbons, the most commonly used of which is dichlorodifluoromethane, are believed to diffuse unchanged from the earth's surface where they are released, to the upper levels of the atmosphere. Here they encounter short wavelength ultra-violet radiation and suffer photodissociation. The products of this photochemical reaction are then supposed to interact with the ozone present in the stratosphere and reduce its concentration. As a result ultra-violet light, which would normally be absorbed by the ozone, could reach the ground level and it is claimed increase the incidence of human skin cancer. There is thus, considerable interest in studies of reactions of the products of photolysis of halocarbons. In the case of

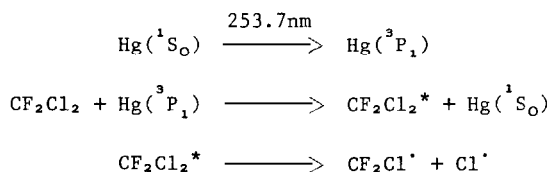
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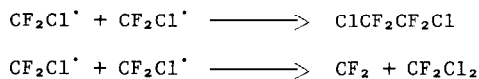
dichlorodifluoromethane the primary products of photolysis are the chlorodifluoromethyl radical and a chlorine atom.



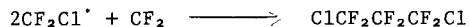
The present paper is concerned with reactions of chlorodifluoromethyl radicals. In earlier studies it was shown that they could be produced directly from dichlorodifluoromethane by the process of mercury photosensitisation, the process being identified by kinetic measurements of mercury vapour consumption [2] and from studies using a monoisotopic mercury lamp [3] as an excited molecule decomposition, comparable with the process of direct photolysis mentioned previously.



In the absence of a suitable substrate chlorodifluoromethyl radicals have been shown to undergo both combination and disproportionation reactions



with the production of 1,2-dichlorotetrafluoroethane and difluoromethylene. The latter compound is a diradical which may react with further chlorodifluoromethyl radicals to form 1,3-dichlorohexafluoropropane.



Both the halogenated ethane and the propane are equally susceptible to mercury photosensitisation (and presumably direct photolysis) with the production of halogenated ethyl and propyl radicals. These larger radicals can also undergo the reactions of combination and disproportionation, so that the results of the prolonged photolysis or sensitisation of dichlorodifluoromethane is the production of halocarbons of ever increasing molecular weight.

Such reactions are however likely to be unimportant in the upper atmosphere because of the low concentrations of dichlorodifluoromethane and the consequent low concentration of chlorodifluoromethyl radicals. It is more likely that the radicals will disappear by interaction with suitable

substrate molecules containing hydrogen, present in the upper atmosphere, such as methane or water. Earlier studies have revealed that chlorodifluoromethyl radicals readily abstract hydrogen atoms at room temperature both from hydrocarbons [4] and from halohydrocarbons [5].



The energy of activation for the abstraction reaction varies widely with the nature of  $\text{R}^\cdot$  and in the present work the effect of introducing heteroatoms into  $\text{R}^\cdot$  on the rate of hydrogen abstraction and the energy of activation is examined.

1,3-dichlorotetrafluoroacetone has been shown to be an efficient source of chlorodifluoromethyl radicals when it is photolysed with ultra-violet light at a wavelength close to its absorption maximum at 313 nm. The rate of recombination of chlorodifluoromethyl radicals has been determined by the use of the sector technique and so it is possible to measure the Arrhenius parameters for abstraction by photolysing mixtures of the ketone and substrate molecules in the gas phase and analysing the products.

## EXPERIMENTAL

### Materials

1,3-dichlorotetrafluoroacetone was obtained from Koch Light Ltd. It was purified by bulb-to-bulb distillation over  $\text{P}_2\text{O}_5$  on a vacuum line and its purity checked by mass spectrometry. Dimethyl ether and trimethylamine were obtained from Cambrian Chemicals Ltd and were used without further purification. Tetramethylsilane was obtained from Prochem Ltd. It was distilled before use and its purity checked by gas chromatography and mass spectrometry.

### Procedure

Gas mixtures of measured pressures of 1,3-dichlorotetrafluoroacetone and substrate molecules were made using a conventional vacuum line and were photolysed in quartz vessels of 38 cm<sup>3</sup> capacity, housed in an aluminium block furnace. The light source was a medium pressure mercury vapour lamp, Phillips HPK 125 W, and was collimated with a pair of quartz lenses to form a parallel beam through the cell. The line at 313 nm was isolated by means of a filter assembly consisting of a Chance OX7 filter, 1 cm of potassium

hydrogen phthalate solution ( $4 \text{ g dm}^{-3}$ ), 1 cm of potassium chromate ( $0.2 \text{ g dm}^{-3}$ ) and 4 cm of saturated nickel sulphate solution ( $440 \text{ g dm}^{-3}$  of the anhydrous salt). The light passing through the reaction cell was monitored by a photocell galvanometer combination.

After photolysis the contents of the cell were frozen into a U-tube with liquid air and the carbon monoxide pumped to a McLeod gauge for measurement. The concentration of carbon monoxide was taken as a measure of the extent of photolysis. The contents of the U-tube were then vapourised and passed to the inlet system of a gas chromatograph for analysis.

The products of photolysis were separated using a combination of a short activated alumina column,  $15 \text{ cm} \times 0.6 \text{ cm}$  and a 40:60 mesh Celite column,  $600 \text{ cm} \times 0.6 \text{ cm}$ , coated with 15% Kel F No.3 oil. The flow of nitrogen carrier gas was  $1.5 \text{ dm}^3/\text{hr}$  and detection was by means of a katharometer. For quantitative work the chromatographic peak areas of the photolysis products were compared with those obtained from known pressures of authentic samples. In some runs the products were examined directly by mass spectrometry using an AEI MS902 mass spectrometer.

## RESULTS AND DISCUSSION

The abstraction of hydrogen atoms by  $\text{CF}_2\text{Cl}^\cdot$  radicals was studied by photolysing a gas mixture of 1,3-dichlorotetrafluoroacetone ( $2.2 \times 10^{-6} \text{ mol cm}^{-3}$ ) and an appropriate concentration of the substrate molecule for periods of up to 3 hr at a variety of temperatures in the range 293 - 468 °K. The rates of formation of 1,2-dichlorotetrafluoroethane and chlorodifluoromethane were measured and the rate constant for the abstraction reaction  $k_A$  derived, using the relation

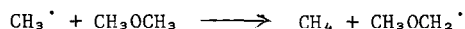
$$\frac{\text{Rate}_{\text{CF}_2\text{ClH}}}{\text{Rate}_{\text{C}_2\text{F}_4\text{Cl}_2}} = \frac{k_A}{k_C^2} [\text{RH}]$$

where RH is the substrate molecule and  $k_C$  the rate constant for the recombination of  $\text{CF}_2\text{Cl}^\cdot$  radicals. An Arrhenius plot of  $\log k_A$  against  $1/T$  was constructed and a least mean squares treatment of the data used to derive a value for  $E_A$ , the energy of activation for the abstraction reaction and for  $A_A$ , the pre-exponential factor.

The effect of including a hetero-atom within the substrate molecule on the Arrhenius parameters for the hydrogen abstraction reaction was examined by selecting as substrate molecules dimethyl ether, trimethylamine and tetramethylsilane. In each molecule the hetero-atom is in an equivalent position with respect to the hydrogen atom which is lost. Any change in the energy of activation will therefore reflect a change in the (C-H) bond dissociation energy, but the value of  $E_A$  should not be affected by the number of hydrogen atoms available for abstraction within the molecule.

### Dimethyl ether

The abstraction of hydrogen atoms from dimethyl ether by methyl radicals has been studied by a number of workers and the results obtained vary to some extent with the source of the methyl radicals. This discrepancy may be due to uncertainties about the course of the reaction because of the possibility of the removal of hydrogen atoms from the radical source, rather than the substrate molecule dimethyl ether. The values obtained for the Arrhenius parameters of the reaction



are compared in Table 1. In one case the uncertainty about the origin of the abstracted hydrogen atom is removed by using a deuterated radical source. When the methyl radical is replaced by a trifluoromethyl radical the energy of activation for hydrogen abstraction falls significantly, reflecting the higher (C-H) bond dissociation energy in trifluoromethane.

TABLE 1

Arrhenius parameters for the abstraction of hydrogen from dimethyl ether

Radical	$E_A$ kJ mol <sup>-1</sup>	$\log_{10} A_A$	Radical source	Reference
CH <sub>3</sub>	39.7 ± 0.8	11.5	CH <sub>3</sub> COCH <sub>3</sub>	6
CH <sub>3</sub>	35.1 ± 6	11.0	Hg(CH <sub>3</sub> ) <sub>2</sub>	7
CH <sub>3</sub>	41.4 ± 8.4	11.8	CH <sub>3</sub> OCH <sub>3</sub> -H	8
CD <sub>3</sub>	45.1 ± 4.2	-	CD <sub>3</sub> CDO	9
CH <sub>3</sub>	39.3	11.04	CH <sub>3</sub> OCH <sub>3</sub> Hg <sup>*</sup>	10
CH <sub>3</sub>	41.4 ± 0.7	11.62 ± 0.08	CH <sub>3</sub> COCH <sub>3</sub>	11
CF <sub>3</sub>	28.3 ± 0.2	11.71 ± 0.03	CF <sub>3</sub> COCF <sub>3</sub>	12
CF <sub>2</sub> Cl	17.5	11.3 ± 0.2	CF <sub>2</sub> ClCOCF <sub>2</sub> Cl	this work

The results obtained from the photolysis of mixtures of 1,3-dichlorotetrafluoroacetone and dimethyl ether are summarised in Table 2. The value of  $E_A$ , the energy of activation for the reaction  $CF_2Cl' + CH_3OCH_3 \rightarrow CF_2ClH + CH_3OCH_2'$  was calculated using a least mean squares treatment of the data to be  $17.5 \pm 0.4$  kJ mol<sup>-1</sup>. This value is lower than would be anticipated from a comparison of the (C-H) bond dissociation energy in CF<sub>3</sub>H and CF<sub>2</sub>ClH, but it is of the same order as that obtained for the abstraction of hydrogen from cyclopentane with CF<sub>2</sub>Cl' radicals (22.1 kJ mol<sup>-1</sup>).

TABLE 2

Abstraction of hydrogen from dimethyl ether by CF<sub>2</sub>Cl' radicals

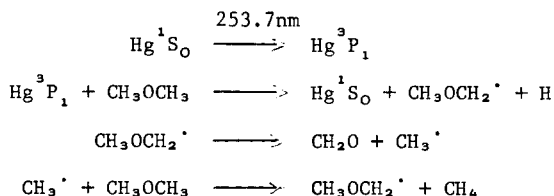
Temperature °K	Rate CF <sub>2</sub> ClH mol cm <sup>-3</sup> s <sup>-1</sup> × 10 <sup>12</sup>	Rate C <sub>2</sub> F <sub>4</sub> Cl <sub>2</sub> mol cm <sup>-3</sup> s <sup>-1</sup> × 10 <sup>12</sup>	k <sub>A</sub> /k <sub>C</sub> <sup>1/2</sup>
293	32.0	25.8	31.5
305	38.0	27.9	35.8
335	202.0	38.8	161.6
353	173.0	32.0	153.0
373	181.0	24.1	184.7
385	198.0	23.4	204.5
403	254.0	15.5	323.2
423	279.0	13.1	386.4
456	329.0	11.8	480.1
463	349.0	11.6	511.7

Concentration of dimethyl ether =  $2.0 \times 10^{-7}$  mol cm<sup>-3</sup>

Concentration of 1,3-dichlorotetrafluoroacetone =  $2.2 \times 10^{-6}$  mol cm<sup>-3</sup>

The value obtained for the pre-exponential factor  $\log_{10} A = 11.3 \pm 0.2$  and this is lower than that obtained for abstraction by either CF<sub>3</sub> or CH<sub>3</sub> radicals and suggests the intervention of secondary reactions. In a study of the abstraction of hydrogen from diethyl ether by methyl radicals obtained by the photolysis of acetone, Trotman Dickenson and Steacie [6] showed that the reaction mechanism was complicated by the decomposition of the ethoxyethyl radical into acetaldehyde and ethylene. A similar

decomposition of the methoxymethyl radical obtained in the present system has been postulated:  $\text{CH}_3\text{OCH}_2^\cdot \rightarrow \text{CH}_2\text{O} + \text{CH}_3^\cdot$ . The importance of this reaction at the temperatures used in the present work may be assessed from thermochemical data. The heat of formation of the methoxymethyl radical is not known but may be calculated using the relation  $D(\text{CH}_3\text{OCH}_2\text{-H}) = \Delta H_f(\text{H}) + \Delta H_f(\text{CH}_3\text{OCH}_2^\cdot) - \Delta H_f(\text{CH}_3\text{OCH}_3)$  and known values of the (C-H) bond dissociation energy in dimethyl ether (388.7 kJ mol<sup>-1</sup>) and the heats of formation of the hydrogen atom (217.4 kJ mol<sup>-1</sup>) and of dimethyl ether (-183.9 kJ mol<sup>-1</sup>). The calculated value ( $\Delta H_f \text{CH}_3\text{OCH}_2^\cdot = -12.6$  kJ mol<sup>-1</sup>) may now be combined with the known heats of formation of formaldehyde (-61 kJ mol<sup>-1</sup>) and the methyl radical (142.1 kJ mol<sup>-1</sup>) to derive a value for the heat of dissociation ( $\Delta H$ ) of the methoxymethyl radical  $\text{CH}_3\text{OCH}_2^\cdot \rightarrow \text{CH}_2\text{O} + \text{CH}_3^\cdot$  using the relation  $\Delta H = \Delta H_f(\text{CH}_2\text{O}) + \Delta H_f(\text{CH}_3^\cdot) - \Delta H_f(\text{CH}_3\text{OCH}_2^\cdot)$ . The value obtained for  $\Delta H$  is 93.7 kJ mol<sup>-1</sup> and the correctness of this analysis may be checked by considering the case of the mercury photo-sensitisation of dimethyl ether. The mechanism for this process, which leads to the formation of formaldehyde and methane, was shown to be [10]:



The energy transferred from the excited mercury atoms to the dimethyl ether molecules upon collision is 480.7 kJ mol<sup>-1</sup>. The energy remaining within the methoxymethyl radical can be estimated by subtracting the (C-H) bond dissociation energy from this value. The resulting estimate of 92 kJ mol<sup>-1</sup> is close to the value of 93.7 kJ mol<sup>-1</sup> calculated for  $\Delta H$  so that the agreement is satisfactory. The energy of activation for the decomposition of the methoxymethyl radical must thus exceed 92 kJ mol<sup>-1</sup> and so secondary reactions resulting from the dissociation of methoxymethyl radicals would be unimportant at the temperatures used in the present work. An examination of the products of photolysis by mass spectrometry at the highest temperature reported here revealed only slight traces of formaldehyde and methane.

Trimethylamine

The abstraction of hydrogen atoms from trimethylamine by methyl radicals has been studied by photolysing mixtures of acetone and trimethylamine. It can be seen from Table 3 that there is some disagreement between different groups of workers on the exact value for the energy of activation. This disagreement is not due to any uncertainty in the origin of the hydrogen atom abstracted, for a parallel study using hexadeuteroacetone gives a result of the same order. As in the case of dimethyl ether, the energy of activation for hydrogen abstraction by trifluoromethyl radicals is much lower, reflecting the increased (C-H) bond strength in trifluoromethane.

TABLE 3

Arrhenius parameters for the abstraction of hydrogen from trimethylamine

Radical	$E_A$ kJ mol <sup>-1</sup>	$\log_{10} A_A$	Radical source	Reference
CH <sub>3</sub>	33.4	11.4	CH <sub>3</sub> COCH <sub>3</sub>	15
CH <sub>3</sub>	37.2 ± 0.4	11.9 ± 0.1	CH <sub>3</sub> COCH <sub>3</sub>	16
CD <sub>3</sub>	36.7 ± 1.6	11.8	CD <sub>3</sub> COCD <sub>3</sub>	6
CF <sub>3</sub>	18.8 ± 0.8	11.82 ± 0.12	CF <sub>3</sub> I	17
CF <sub>2</sub> Cl	15.9	10.6 ± 0.12	CF <sub>2</sub> ClCOCF <sub>2</sub> Cl	this work

The results of the photolysis of mixtures of trimethylamine and 1,3-dichlorotetrafluoroacetone are given in Table 4. A least mean squares treatment of the data gives a value for the energy of activation  $E_A$  of 15.9 kJ mol<sup>-1</sup>. Once again this is lower than the corresponding value for abstraction by trifluoromethyl radicals. A comparison of the values for the energies of activation for the abstraction of hydrogen from dimethyl ether and from trimethylamine shows that for all three radicals (CH<sub>3</sub>, CF<sub>3</sub> and CF<sub>2</sub>Cl)  $E_A$  is lower for trimethylamine than for dimethyl ether. This is not due to the increased number of hydrogen atoms available within the molecule and must be attributed to a difference in the (C-H) bond dissociation energy. This is supported by comparing the value of  $E_A$  for the abstraction of hydrogen from cyclopentane by CF<sub>2</sub>Cl radicals (22.1 kJ mol<sup>-1</sup>).



This is greater than that for either dimethyl ether or trimethylamine although the number of hydrogen atoms exceeds those in either substrate. There is, however, some evidence that the rate constant is affected by the number of available hydrogen atoms and earlier workers have shown that it rises in the series  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$  and  $(\text{CH}_3)_3\text{N}$ . The ratio of rate constants for the abstraction of hydrogen (attached to the carbon atom) from these three substrates is 1:3:6 for methyl radicals and 1:4.5:10 for trifluoromethyl radicals [13].

TABLE 4

Abstraction of hydrogen from trimethylamine by  $\text{CF}_2\text{Cl}^\cdot$  radicals

Temperature °K	Rate $\text{CF}_2\text{ClH}$ $\text{mol cm}^{-3} \text{ s}^{-1} \times 10^{12}$	Rate $\text{C}_2\text{F}_4\text{Cl}_2$ $\text{mol cm}^{-3} \text{ s}^{-1} \times 10^{12}$	$k_A/k_C^{1/2}$
343	57.9	6.67	71.8
393	64.7	5.61	87.7
408	70.8	6.45	89.9
421	74.6	5.05	107.9
433	71.9	4.04	114.8
437	73.1	3.19	132.5
447	147.0	12.62	133.6

Concentration of trimethylamine =  $3.1 \times 10^{-7} \text{ mol cm}^{-3}$

Concentration of 1,3-dichlorotetrafluoroacetone =  $2.2 \times 10^{-6} \text{ mol cm}^{-3}$

The value for the pre-exponential factor  $\log_{10} A_A = 10.6$  is lower than expected, but it is not possible to estimate the importance of secondary reactions because of the lack of reliable thermochemical data, however, it can be assumed that decomposition of the secondary radical will take place at higher temperatures with the formation of methyl methylene imine and a methyl radical



Similar decompositions have been observed in the pyrolysis of tetramethyl urea [14] and dimethyl formamide [14]. An examination of the products of photolysis at high temperature by mass spectrometry yielded only a trace of

the anticipated methyl methylene imine, suggesting that secondary reactions are unimportant in the temperature range studied.

#### Tetramethyl silane

The abstraction of hydrogen from tetramethyl silane by methyl radicals has been studied by several groups of workers using alternative radical sources. The values calculated for the energy of activation  $E_A$  vary to some extent, but this uncertainty is not due to differences in the origin of the abstracted hydrogen atom. The results obtained using trideuteromethyl radicals derived from hexadeuteroacetone or hexadeuteroazomethane are of the same order as those obtained using methyl radicals, as shown in Table 5.

TABLE 5

Arrhenius parameters for the abstraction of hydrogen from tetramethyl silane

Radical	$E_A$ kJ mol <sup>-1</sup>	$\log_{10} A_A$	Radical source	Reference
CH <sub>3</sub>	40.6	11.34	CH <sub>3</sub> N <sub>2</sub> CH <sub>3</sub>	18
CD <sub>3</sub>	44.8	11.91	CD <sub>3</sub> N <sub>2</sub> CD <sub>3</sub>	22, 25
CH <sub>3</sub>	46 ± 1.2	12.6 ± 0.2	CH <sub>3</sub> N <sub>2</sub> CH <sub>3</sub>	19
CH <sub>3</sub>	43	11.53	CH <sub>3</sub> N <sub>2</sub> CH <sub>3</sub>	20, 21
CH <sub>3</sub>	42.8	11.55	CH <sub>3</sub> N <sub>2</sub> CH <sub>3</sub>	13
CD <sub>3</sub>	43.3	11.84	CD <sub>3</sub> COCD <sub>3</sub>	13
CD <sub>3</sub>	45.1	12.0	CD <sub>3</sub> COCD <sub>3</sub>	22
CF <sub>3</sub>	30.2	11.88	CF <sub>3</sub> COCF <sub>3</sub>	13
CF <sub>3</sub>	31.8	12.0	CF <sub>3</sub> I	23
CF <sub>3</sub>	30.5	11.91	CF <sub>3</sub> COCF <sub>3</sub>	24
C <sub>2</sub> F <sub>5</sub>	29.3	11.15	C <sub>2</sub> F <sub>5</sub> COC <sub>2</sub> F <sub>5</sub>	25
CF <sub>2</sub> Cl	20.3	11.95 ± 0.22	CF <sub>2</sub> ClCOCF <sub>2</sub> Cl	this work

When the methyl radical is replaced by a trifluoromethyl radical once again there is a fall in the value for  $E_A$  of about 10 kJ. This is approximately the same as that observed for the other two substrate molecules,

dimethyl ether and trimethylamine. The value of  $E_A$  obtained for abstraction from tetramethyl silane is approximately the same whether the radical source is hexafluoroacetone or trifluoromethyl iodide. There is a further small fall in the value of  $E_A$  when the trifluoromethyl radical is replaced by the pentafluoroethyl radical. It is unlikely that this is due to any difference in the (C-H) bond dissociation energy in trifluoromethane and pentafluoroethane.

The results of the study of the photolysis of mixtures of tetramethyl silane and 1,3-dichlorotetrafluoroacetone are given in Table 6. A least mean squares treatment of the data gives a value for the energy of activation  $E_A$  for the abstraction of hydrogen from tetramethyl silane by  $CF_2Cl'$  radicals of  $20.3 \text{ kJ mol}^{-1}$ . This is again lower than that obtained for abstraction by trifluoromethyl radicals from tetramethyl silane, but higher than that obtained for abstraction by  $CF_2Cl'$  radicals from either dimethyl ether or trimethylamine. There is thus a close parallel in the variation of  $E_A$  with the nature of the substrate molecule for all three radicals and this must reflect a variation in the (C-H) bond dissociation energy due to the effect of the hetero atom. As anticipated the number of available hydrogen atoms within the molecule has no effect on  $E_A$ .

TABLE 6

Abstraction of hydrogen from tetramethyl silane by  $CF_2Cl'$  radicals

Temperature °K	Rate $CF_2ClH$ $\text{mol cm}^{-3} \text{ s}^{-1} \times 10^{12}$	Rate $C_2F_4Cl_2$ $\text{mol cm}^{-3} \text{ s}^{-1} \times 10^{12}$	$k_A /$ $k_C^{\frac{1}{2}}$
303	53.0	7.55	126.4
327	65.0	6.58	165.3
343	121.0	9.10	261.8
376	136.0	5.93	362.8
418.5	186.0	2.90	715.1
435	214	2.32	926.3
469	234	1.18	1403.1

Concentration of tetramethyl silane =  $1.53 \times 10^{-7} \text{ mol cm}^{-3}$

Concentration of 1,3-dichlorotetrafluoroacetone =  $2.2 \times 10^{-6} \text{ mol cm}^{-3}$

In the absence of reliable thermochemical data it is not possible to predict the fate of the secondary radical  $(\text{CH}_3)_3\text{SiCH}_2\cdot$ , but a mass spectrometric examination of the products of photolysis provided no evidence of radical dissociation. The only new compound containing silicon which could be identified was  $(\text{CH}_3)_3\text{SiCH}_2\text{CF}_2\text{Cl}$ .

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