

$$\Delta H_3^\circ = 21.22 \text{ kJ mol}^{-1}$$

$$\Delta H_4^\circ = 166.5 \text{ kJ mol}^{-1}$$

in good agreement with literature data.⁶⁸ The above values support our suggestion that in the β -scission of the alkoxy radicals the formation of CH_3^\bullet is preferable to that of $\dot{\text{C}}\text{N}$.

IV. The heats of formation of rOH and rOOH have been calculated by using group additivity rules:

(68) Kwang Yul Choo; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, *13*, 833.

(69) Van Hook, J. P.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1958**, *80*, 779.

(70) Hammond, G. S.; Sen, J. N.; Boozer, C. E. *J. Am. Chem. Soc.* **1955**, *77*, 3244.

(71) Rubtsov, V. I.; Roginskii, V. A.; Miller, V. B.; Zaikov, G. E. *Kinet. Katal.* **1980**, *21*, 612.

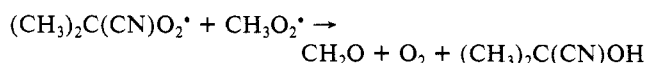
(72) Keszler, A. Ph.D. Thesis, Technical University, Budapest, 1982.

$$\Delta H_f^\circ[(\text{CH}_3)_2\text{C}(\text{CN})\text{OH}] = -178.05 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ[(\text{CH}_3)_2\text{C}(\text{CN})\text{OOH}] = -106.44 \text{ kJ mol}^{-1}$$

On the other hand, if heats of reactions and the value $\Delta H_f^\circ(\text{r}^\bullet)$ taken from the literature^{66,67} are used, similar values can be compiled.

V. Finally, all the above data enable us to calculate the enthalpy change of the cross combination:



being

$$\Delta H_{cc}^\circ = -369.28 \text{ kJ mol}^{-1}$$

Registry No. DTBC, 128-37-0; AIBN, 78-67-1.

Reactions of Trifluoromethyl and Triplet Methylene Radicals with Some Alkylsilanes

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The recombination of CF_3 and CH_2SiF_3 radicals was used to prepare $\text{CF}_3\text{CH}_2\text{SiF}_3$ by collisional stabilization of the initially formed hot molecule, $\text{CF}_3\text{CH}_2\text{SiF}_3^\bullet$. One fate of this hot species, not so far observed, is its decomposition to give CF_3CH_2 and SiF_3 radicals, a process which leads to additional products. In separate studies of the reactions of $^3\text{CH}_2$ with $\text{CF}_3\text{CH}_2\text{SiF}_3$, the formation of CH_3SiF_3 is observed, and this is suggested to be through a 5-coordinate radical exchange process.

Introduction

In previous studies¹ of the reactions of $^3\text{CH}_2$ with some methylfluorosilanes, a radical elimination exchange mechanism was proposed. This present work involving $\text{CF}_3\text{CH}_2\text{SiF}_3$ and $\text{CH}_3\text{-CF}_2\text{SiF}_3$ stems from this proposal and was designed to provide further evidence of the validity of this mechanism.

$\text{CF}_3\text{CH}_2\text{SiF}_3$ was prepared by the recombination reaction of CF_3 with CH_2SiF_3 radicals, a reaction which had earlier been studied during investigations of H atom abstraction by CF_3 radicals from methylfluorosilanes.² Under the reaction conditions of the present work, evidence was obtained for an additional hot molecule reaction of $\text{CF}_3\text{CH}_2\text{SiF}_3^\bullet$ which has not so far been reported. The results are described in this paper.

Reaction of CF_3 with Alkylsilanes

Experiment and Results. Hexafluoroacetone (HFA), obtained from Allied Chemical, and methyltrifluorosilane (MTS), obtained from ICN Pharmaceuticals, were fractionated and stored as previously described.² The materials collected showed no detectable impurities when subject to gas chromatographic analysis.

These materials, 130 Torr of HFA and 290 Torr of MTS, were mixed in a 215-mL quartz reaction vessel maintained at 150 °C. The mixture was irradiated with light from a PEK 200-W high-pressure mercury lamp filtered with a Pyrex filter cell containing water.

Following an irradiation time of 100 min, the cell was opened to traps at -77, -160, and -196 °C. The noncondensable CO , measured in a gas buret, indicated that 60% of the HFA had decomposed.

The fraction condensable at -196 °C was analyzed by gas chromatography and was shown to contain C_2F_6 , CF_2CH_2 , and CF_3H ; this fraction was discarded. The fraction collected at -160 °C contained unreacted HFA and MTS and other products. This

fraction was returned to the reaction vessel along with additional HFA to maintain its partial pressure at approximately 130 Torr. Second and third irradiations were performed in this fashion.

The total fraction collected at -160 °C was separated by preparative gas chromatography involving a 6-ft Porapak P column programmed between 60 and 220 °C. Each peak was collected, and the corresponding NMR and mass spectra were recorded and used to identify the compound. These products are listed below.

The product of main interest, $\text{CF}_3\text{CH}_2\text{SiF}_3$, was produced with a yield of 150 μmol , corresponding to a pressure in the reaction vessel of 13 Torr at 25 °C.

A number of other products were isolated and identified, and these were of sufficient interest to warrant further investigation from a semiquantitative mechanistic point of view. A small amount of a relatively involatile liquid collected at -77 °C was not investigated.

Two sets of experiments were carried out to determine the relative amounts of volatile products formed when HFA was photolyzed with MTS: (a) total pressure, 180 Torr; HFA:MTS = 1:2; quartz reaction vessel; volume, 215 mL; temperature, 150 °C; time, 30 min; (b) as in (a) but with 300 Torr of N_2 added. In each case, the noncondensable products were removed after reaction and then, without fractionation, the reaction mixture was subjected to gas chromatography using a Porapak P column programmed between 60 and 220 °C. Each eluted compound was collected, and its NMR and mass spectra were recorded.

Besides CO , unambiguous identification of the following compounds was obtained: CO_2 , C_2F_6 , CF_3H , CH_2CF_2 , $\text{CF}_3\text{CH}_2\text{SiF}_3$, $\text{CH}_3\text{CF}_2\text{SiF}_3$, $\text{CF}_3\text{CH}_2\text{CF}_2\text{SiF}_3$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{SiF}_3$, and CF_3SiF_3 .

In addition, after standing for a considerable period (≈ 3 days), it was noted that two other products appeared, CF_3CHCF_2 and $\text{CF}_3\text{CH}_2\text{CF}_3$.

(1) Bell, T. N.; Sherwood, A. G. Soto-Garrido, G. *J. Phys. Chem.* **1985**, *89*, 1155.

(2) Bell, T. N.; Zucker, U. F. *J. Phys. Chem.* **1970**, *74*, 979.

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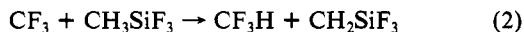
TABLE I: Relative Peak Areas of Products^a

	CF ₃ H	CF ₃ SiF ₃	CH ₂ =CF ₂	CH ₃ CF ₂ SiF ₃	CF ₃ CH ₂ SiF ₃	CF ₃ CH ₂ CF ₂ SiF ₃	CF ₃ CF ₂ CH ₂ SiF ₃
without N ₂	100	0.56	0.40	21	7.2	7.9	1.6
with N ₂	100	0.46	<0.28	18	14	5.0	1.1

^a Reaction conditions: CH₃SiF₃, 120 Torr; HFA, 60 Torr; N₂ (when present), 300 Torr; reaction time, 30 min; temperature, 150 °C.

The results are presented in Table I in terms of the peak area of each product relative to that of CF₃H.

Discussion. The formation of many of the products is well-understood through established free-radical reactions which need not be discussed. Thus, the following reactions are proposed



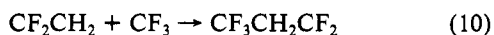
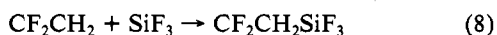
In earlier studies,³ the hot molecule β -fluoro transfer process, (5), was established.



(In reaction 4, M is a third body.) In order to account for CF₃SiF₃ and other silicon-containing products observed in the present study, an additional fate of the hot molecule, CF₃CH₂SiF₃^{*}, appears to be the most logical proposal. That this reaction was not considered in earlier studies is presumably because of a difference in reaction conditions in which the products in question were not formed in amounts sufficient to be identified. A Si-C bond scission, (6),



is proposed as an additional reaction of the hot molecule, followed by a series of facile radical-radical and molecule-radical reactions. Thus, the observed products are accounted for by reactions 7 to 15. A small amount of liquid product, not very volatile at room temperature, was not analyzed. Presumably, this consisted of long-chain fluorocarbons or silicon-containing fluorocarbons formed in free-radical reactions.



Other alternative reactions for the intermediate radicals from (8) and (9) can of course be written. From the ratio CF₃CF₂-CH₂SiF₃:CF₃CH₂CF₂SiF₃ = 1:5 we presume (9) is favored over (8); however, we recognize the same products are also formed through (14) and (15).

If (9) is a favored pathway, we account for the formation of CH₃CF₂SiF₃ through the H abstraction reaction, (16), and this molecular product is observed in good yield.



A simple test of the proposed mechanism would be by the addition of a third body. The silicon-containing products have been proposed to arise from the decomposition of the hot molecule, CF₃CH₂SiF₃^{*}, reaction 6, resulting from the radical combination reaction, (4). Addition of N₂ as a third body should cause sta-

bilization of the hot molecule and thus an increase in the yield of CF₃CH₂SiF₃ from reaction 4. Any increase in reaction 4 will result in a decrease in the extent of reactions 5 and 6 and thus in the yields of products of these reactions. This is indeed indicated in the data of Table I, where it is seen that the addition of N₂ increased the amount of CF₃CH₂SiF₃ and decreased the amounts of those alternative products that could be measured.

Reactions of ³CH₂ with Alkylsilanes

Experiment. Ketene was used as the source of CH₂. It was synthesized from acetone by using a ketene generator and purified by trap-to-trap distillation. The fraction collected at -160 °C was purified by preparative gas chromatography on a Poropak Q column at 90 °C. The ketene was stored at -196 °C, and the required amounts of this compound were purified immediately before use by gas chromatography.

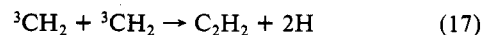
Reaction of ³CH₂ with CF₃CH₂SiF₃. CF₃CH₂SiF₃ was prepared as described above. A mixture of ketene (2 Torr) and CF₃CH₂SiF₃ (12 Torr) at 25 °C in the 215-mL quartz cell was irradiated with the mercury lamp using a Corning 7-37 and 0-52 filter combination. An irradiation time of 1.5 h was chosen so as to decompose approximately 10% of the ketene.

The reaction mixture was then distilled through traps cooled to -160, -196, and -210 °C. The noncondensable fraction (CO) was measured in a gas buret, and the fractions condensed at -196 and -210 °C were combined and analyzed by gas chromatography using a Poropak N column programmed from 50 to 190 °C. This fraction yielded peaks corresponding to CO₂, C₂H₄, C₂H₆, CH₂CF₂, and unreacted ketene.

The fraction condensing at -160 °C contained unreacted silane and other products which were isolated by gas chromatography and identified by NMR and mass spectrometry. These products were CH₂CF₂, CF₃CH₂CF₃, and CF₂CHCF₃. Three unidentified products which did not contain SiF₃ groups were also present in this fraction. Of significance in terms of the mechanism of the reaction was the formation of a small quantity of CH₃SiF₃.

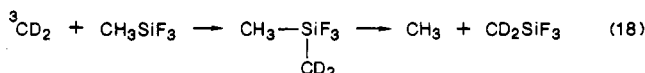
Reaction of ³CH₂ with CH₃CF₂SiF₃. In a similar set of experiments with the α -fluorosilane, the most volatile fraction contained CO₂, C₂H₄, C₂H₆, CF₂CH₂, and unreacted ketene. Only traces of C₂H₂ were formed. The fraction condensed at -160 °C contained CH₂CF₂, CO₂, CF₃CHCF₂, and an unidentified product which did not contain the SiF₃ group.

Discussion. Mechanistic Proposals Involving ³CH₂. Under the experimental conditions, it would be expected that very little ¹CH₂ would be present and most of the CH₂ would be in the triplet state.⁴ The absence of C₂H₂ is consistent with our previous observation¹ whereby the reaction of ³CH₂ with methylfluorosilanes competitively excluded the bimolecular reaction leading to C₂H₂.



This reaction is commonly accepted to occur in the photolysis of ketene.⁵

In previous studies¹ of the reaction of ³CD₂ with methyltri-fluorosilane, the results were interpreted in terms of a 5-coordinate intermediate CH₃(CD₂)SiF₃ being produced, leading to deuterium-hydrogen scrambling and the release of an isotopically scrambled exchange methyl radical.



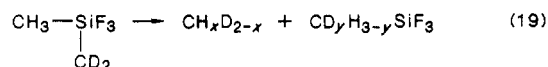
(3) Bell, T. N.; Berkely, R.; Platt, A. E.; Sherwood, A. G. *Can. J. Chem.* 1974, 52, 3158.

(4) Canosamas, C. E.; Frey, H. M.; Walsh, R. J. *J. Chem. Soc., Faraday Trans. 2* 1984, 80, 561.

(5) Russell, R. L.; Rowland, F. S. *J. Am. Chem. Soc.* 1970, 92, 7508.

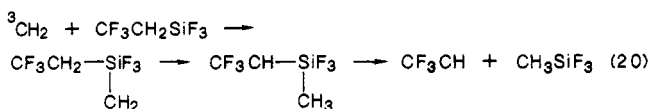
On the basis of isotopic composition of the products, scrambling of H and D in the intermediate was proposed.

An alternative reaction of the intermediate, namely, the reverse of the first step of (18), whereby isotopically scrambled methylene is released, i.e.



could not be detected because of the difficulty of determining small amounts of $\text{CD}_y\text{H}_{3-y}\text{SiF}_3$ in the presence of large amounts of the CH_3SiF_3 starting material.

The present systems allow a more meaningful analysis of this question. Thus, CH_3SiF_3 is detected in the reaction of $^3\text{CH}_2$ with $\text{CF}_3\text{CH}_2\text{SiF}_3$. We propose reaction 20 to account for this, i.e.,

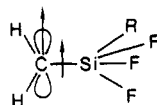


the formation of a 5-coordinate intermediate, intramolecular hydrogen transfer, followed by breakage of a different Si-C bond. We do not observe the formation of CH_3SiF_3 in the reaction of $^3\text{CH}_2$ with $\text{CH}_3\text{CF}_2\text{SiF}_3$. Arguments concerning the mechanistic proposal and experimental observations are below.

(1) An examination of molecular models of the two systems suggests a stereochemical explanation. Intramolecular H atom transfer to the attacking methylene requires the juxtaposition of the H atom being transferred and the singly occupied p orbital of the attached methylene in the 5-coordinate intermediate. The propensity for β -fluoro atoms to coordinate to silicon is well-known, and any such strong interaction in the present case would lock the attacking CH_2 in excellent position relative to the α - CH_2 of the CF_3CH_2 group so that H atom transfer could take place.

In the case of the α -fluoro system, $\text{CH}_3\text{CF}_2\text{SiF}_3$, the locking of the intermediate in this position would not be possible. Indeed, a molecular model of the system suggests that the minimum-energy configuration will have the CH_3 group with maximum separation from the attached CH_2 , thus reducing the possibility of H atom transfer.

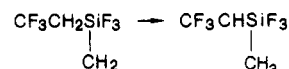
(2) If the intermediate is formally considered to have the electron distribution



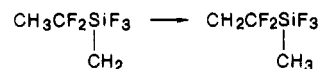
H atom transfer with a neighboring group, R, may be likened to a free-radical type of process. The β -fluorine atom exhibits strong coordination to an empty d orbital of the central Si atom. This

would markedly enhance the electron density on the Si atom and thus the free-radical nature of the CH_2 group. Such an influence would be expected to favor H atom transfer from the $-\text{CH}_2\text{CF}_3$ group relative to the $-\text{CF}_2\text{CH}_3$ group.

(3) Energetic arguments may also be applied. The process



proposed for the 5-coordinate intermediate is favored in the forward over the reverse direction when the nature of the radicals is considered. Thus, forward involves primary to secondary radical conversion while reverse is secondary to primary. It is the product of the forward reaction which is required for the pathway leading to CH_3SiF_3 formation. By contrast, the reaction

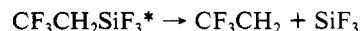


involves primary to primary radical changes in each direction, a less energetically attractive proposition than that above.

The alternative to CH_3SiF_3 formation is the elimination of R. This was not investigated in the present work except to note that fluorocarbon products were observed.

Conclusions

(a) An extended investigation of the products formed in the reaction of CF_3 radicals with CH_3SiF_3 has led to the suggestion of a new mode of decomposition of a hot molecule formed during the process, viz.



We propose that this process is responsible for the formation of a range of silicon-containing products due to subsequent reactions of the SiF_3 radical.

(b) The present results with $^3\text{CH}_2$, together with those previously reported,¹ are compatible with the idea of a 5-coordinate intermediate being formed when $^3\text{CH}_2$ attacks a four-coordinate silicon system. Intramolecular H atom transfer may then occur within this intermediate between the attached CH_2 group and a H atom within the intermediate structure. The final step in the process leads to a 4-coordinate Si system, again through cleavage of one of the Si-C bonds. This yields two options, either carbene + silane or alkyl radical + radical silane system.

Acknowledgment. We thank the National Science and Engineering Research Council for financial support and Dr. Ross Hill for helpful discussion.

Registry No. HFA, 684-16-2; MTS, 373-74-0; $\text{CF}_3\text{CH}_2\text{SiF}_3$, 54389-21-8; $^3\text{CH}_2$, 2465-56-7; F_3C , 2264-21-3; ketene, 463-51-4.