Hot molecules in radical combination

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1:1 Difluoroethylene is formed when CF_3 radicals react with alkyl silanes. We propose that the olefin results from the rearrangement and decomposition of a hot molecule arising from radical recombination

$$CF_3 + CH_2SiX_3 \rightarrow CF_3CH_2SiX_3^* \begin{matrix} \xrightarrow{M} CF_3CH_2SiX_3 \\ \searrow CF_2CH_2 + FSiX_3 \end{matrix}$$

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In the presence of the alkylsilanes $(CH_3)_4Si$, $(CH_3)_2SiF_2$, and CH_3SiF_3, the photolysis of hexafluoroacetone (HFA) leads to the expected radical products CF_3H and C_2F_6, but in addition, some CF_2CH_2 is formed. We suggest that this does not arise from a reaction involving excited HFA* with the silanes, from the following evidence: (*a*) The emission spectrum of HFA is not quenched but slightly enhanced by the silanes, in a manner similar to third bodies such as CO_2 (1). (*b*) Addition of sufficient oxygen to quench ^{3}HFA (2) does not suppress the CF_2CH_2 to zero, some 16 mm O_2 being required to eliminate this product. While this does not eliminate ^{1}HFA*, it does suggest that oxygen is acting as a radical scavenger. (*c*) CF_2CH_2 is still formed when the pyrolysis and photolysis of hexafluoroazomethane is used as a radical source.

The CF_2CH_2 is therefore considered to arise from some reaction involving CF_3 radicals. Hydrogen abstraction will lead to CH_2SiX_3 radicals, and the following recombination is possible.

[1] $$CF_3 + CH_2SiX_3 \rightarrow CF_3CH_2SiX_3$$
(X = Me and/or F)

F atoms in a position β to silicon are known to be labile (3*a*, *b*), leading to the thermal unimolecular elimination [2].

[2] $$CF_3CH_2SiX_3 \xrightarrow{\text{Heat}} CF_2CH_2 + FSiX_3$$

In Fig. 1 is plotted the amount of CF_2CH_2 formed when HFA, 60.5 mm, and CH_3SiF_3, 210 mm, were photolyzed for 1 min at 204°, and the reaction mixture then allowed to stand at 204° in the dark for varying periods. It is clear that $R_{CF_2CH_2}$ during photolysis is considerably greater than that formed in the dark reaction. The amount of CO, CF_3H, and C_2F_6 showed no change during this thermal reaction. SiF_4 was also found (infrared and mass spectra). No reaction products were formed on heating the reaction mixture without a period of photolysis.

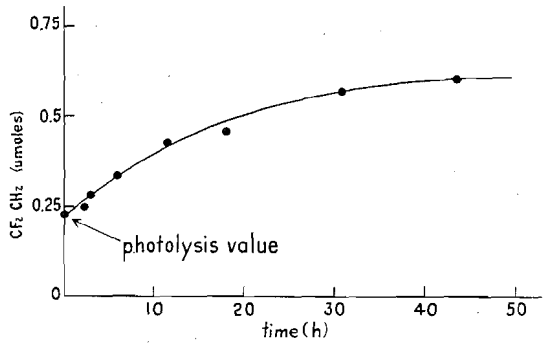

FIG. 1. Amount of CF_2CH_2 formed against time for a photolysis time of 60 s (P_{HFA} 60.5 mm; $P_{CH_3SiF_3}$, 210 mm; temperature, 204°).

In order to explain these results we suggest the formation of a hot molecule in the recombination reaction [3], which leads to the CF_2CH_2 formed during photolysis, reaction [4*b*].

[3] $$CF_3 + CH_2SiF_3 \rightarrow CF_3CH_2SiF_3^*$$

This may be stabilized or decomposed according to reactions [4*a*] and [4*b*],

[4*a*] $$CF_3CH_2SiF_3^* \xrightarrow{M} CF_3CH_2SiF_3$$

[4*b*] $$CF_3CH_2SiF_3^* \rightarrow CF_2CH_2 + SiF_4$$

The dark reaction leading to the much slower $R_{CF_2CH_2}$ is ascribed to the thermolysis [5].

[5] $$CF_3CH_2SiF_3 \rightarrow CF_2CH_2 + SiF_4$$

The absence of products expected from methyl radicals, allows us to ignore elimination from CF_3CH_3* as a source of CF_2CH_2 (*4a, b*).

If the other reactions of CF_3 radicals are hydrogen abstraction, and recombination [6] and [7]

[6] $$CF_3 + CH_3SiF_3 \rightarrow CF_3H + CH_2SiF_3$$

[7] $$CF_3 + CF_3 \rightarrow C_2F_6$$

then, provided reaction [5] goes to completion, $CO = C_2F_6 + \frac{1}{2}CF_3H + \frac{1}{2}CF_2CH_2$. After 43.5 h, we have, as shown in Fig. 1

$$3.75_{(CO)} = 2.95_{(C_2F_6)} + 0.45_{(\frac{1}{2}C_2F_6)} + 0.30_{(\frac{1}{2}CF_2CH_2)} \quad \text{(amounts in μmole)}$$

The CF_3 discrepancy immediately after photolysis is thus recovered during the dark reaction.

A first order Guggenheim plot of the pyrolysis results in Fig 1 gives a good straight line from which $k_5 = 1.6 \times 10^{-5}\ s^{-1}$.

Assuming $A_5 \sim 10^{12}$ yields $E_5 \sim 37$ kcal in agreement with Arrhenius parameters for similar decompositions (*3b*). The hot molecule formed in reaction [3] thus has a large enough excess energy to decompose, assuming the new C—C bond to have a strength ~ 85 kcal.

From reactions [*4a*] and [*4b*], we obtain

[8] $$R_{4a}/R_{4b} = k_{4a}[M]/k_{4b}$$

$R_{4a}/R_{4b} \simeq CF_2CH_2$ (total from pyrolysis)/CF_2CH_2 (photolysis)

The pressure dependence of this ratio is shown below for experiments with photolysis times of 2 min at 200°. The dark decomposition was carried out at higher temperatures. The linear relationship predicted by eq. [8] is not observed. Using the arguments of Pritchard (*5a, b*) this could be ascribed to different collisional efficiencies of the two molecules, and multistep deactivation in reaction [*4a*].

TABLE I

Pressure dependence of R_{4a}/R_{4b}

Pressure of M (mm)		
HFA	CH_3SiF_3	R_{4a}/R_{4b}
60.5	210	1.74
116	69	0.76
49.5	70.5	0.67
38.2	48.7	0.30
30.0	30.0	0.15
10.0	20.0	0.06
4.9	10.6	0.09

Elimination reactions from hot molecules formed from radical recombination have been shown to be important (*4a, b*; *5a, b*). In our case both rearrangement, presumably through the silicon d orbitals, and elimination occur, and exemplify a new type of process.

It is intended to make a full study of this reaction, and extend the work to systems containing boron, germanium, and tin.

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