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Radical Exchange in the Reaction of CF_3 Radicals with Organometallic Compounds

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Summary A radical exchange reaction occurs when CF_3 radicals react with some main-group organometallic compounds; for the system $CF_3 + SnMe_4$ $k_{exch} = 10^7$ ml m^{-1} s^{-1}.

Rebbert and Ausloos[1] reported the exchange of methyl radicals in the system $CH_3 + Hg(CH_3)_2$. We have found that methane, ethane, and 1,1,1-trifluoroethane are formed in the reaction of CF_3 radicals with the methyls of B, Si, Ge, and Sn; this suggests that methyl radicals may be produced. If methyl radicals are formed, then the combination reactions (1), (2), and (3) would be expected to occur.

$$CF_3 + CF_3 \rightarrow C_2F_6 \qquad (1)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (2)$$

$$\begin{tikzcd}
CH_3 + CF_3 \arrow[r] & (CF_3CH_3)^* \arrow[r, "M"] \arrow[rd] & CF_3CH_3 \quad (3) \\
 & & CF_2CH_2 + HF \quad (4)
\end{tikzcd}$$

From (1), (2), and (3), $\Phi = R_{CF_3CH_3}/R^{\frac{1}{2}}_{C_2H_6}R^{\frac{1}{2}}_{C_2F_6}$

In the case of $SiMe_4$ and $GeMe_4$, the amounts of products were too small for quantitative analysis, and the analysis of CF_3CH_3 in the presence of large amounts of BMe_3 proved impossible. Full analysis was possible in the case of the system $CF_3 - SnMe_4$. Thus at 150°, in the presence of 30 mm Hg of hexafluoroacetone (radical source), and 30 mm Hg of $SnMe_4$, $R_{CF_3CH_3} = 2{\cdot}1$, $R_{C_2F_6} = 3{\cdot}2$, $R_{C_2H_6} = 1{\cdot}5$, (mole ml^{-1} $s^{-1} \times 10^{12}$). Thus experimentally $\Phi = 1{\cdot}0$. While this figure is impossible to compare directly with the results of Giles and Whittle,[2] who used the acetone + hexafluoroacetone system, the value is such as to support our suggestion that the C_2F_6, C_2H_6, and CF_3CH_3, occur by reactions (1), (2), and (3).

In the presence of $SnMe_4$, we expect methyl radicals to produce methane by reaction (5).

$$CH_3 + SnMe_4 \rightarrow CH_4 + CH_2SnMe_3 \qquad (5)$$

Thus $k_5 = R_{CH_4} \cdot k_2^{\frac{1}{2}}/R^{\frac{1}{2}}_{C_2H_6}[SnMe_4]$.

Experimentally at 150° using 30 mm Hg of hexafluoroacetone (radical source) and 30 mm Hg of $SnMe_4$, we obtained $R_{C_2H_6} = 1{\cdot}5 \times 10^{-12}$ and $R_{CH_4} = 1{\cdot}8 \times 10^{-12}$ mole ml^{-1} s^{-1}, thus yielding a value for $k_5 = 5{\cdot}9 \times 10^6$ ml m^{-1} s^{-1}. Gowenlock[3] has independently measured k_5 (150°) $= 5 \times 10^6$ ml m^{-1} s^{-1}. We suggest the experimental evidence strongly supports the suggestion that the methyl products result from methyl radicals.

We have shown that methyl products are not obtained if $SnMe_4$ and hexafluoroacetone are heated, nor if $SnMe_4$ is photolysed under the experimental conditions. We suggest that methyl radicals are formed by a radical exchange process (6):

$$CF_3 + SnMe_4 \rightleftarrows (CF_3SnMe_4) \rightarrow CH_3 + CF_3SnMe_3 \qquad (6).$$

Thus methyl radicals are produced at the expense of CF_3 radicals, and if the photolysis of hexafluoroacetone is expressed by

$$(CF_3)_2CO \xrightarrow{h\nu} 2CF_3 + CO$$

a material balance should hold, such that

$$CO = \tfrac{1}{2}CF_3 + \tfrac{1}{2}CH_3 \qquad (7).$$

The volatile products of the reaction between CF_3 radicals and the organometallics are C_2F_6, C_2H_6, CF_3CH_3, CF_2CH_2, CH_4, and CF_3H. The CF_2CH_2 is produced in (4); however, the pressure- and temperature-dependent characteristics of its formation, plus its formation in the dark following periods of photolysis, are indicative of a hot-molecule β-fluoro-rearrangement–elimination reaction, and a thermal reaction occurring, as found in the analogous silicon systems.[4] Thus in the specific case of $CF_3 + SnMe_4$ we have (8), (9), (10), and (11).

$$CF_3 + CH_2SnMe_3 \rightarrow (CF_3CH_2SnMe_3)^* \qquad (8)$$

$$\begin{tikzcd}(CF_3CH_2SnMe_3)^* \arrow[r, "M"] \arrow[dr] & CF_3CH_2SnMe_3 \qquad (9) \\ & CF_2CH_2 + FSnMe_3 \qquad (10)\end{tikzcd}$$

$$CF_3CH_2SnMe_3 \xrightarrow{\text{heat}} CF_2CH_2 + FSnMe_3 \qquad (11)$$

From the data of Whittle[2] on the CF_3CH_3/CF_2CH_2 ratios resulting from reactions (3) and (4), we have selected a value of 2·2 for this ratio under conditions approximating to those of the present work. Thus we can calculate the amount of CF_2CH_2 resulting from (a) reaction (4) and (b) reactions (10) and (11), from a knowledge of the total CF_2CH_2 formed. The CF_3H results from the abstraction reaction (12)

$$CF_3 + SnMe_4 \rightarrow CF_3H + CH_2SnMe_3 \qquad (12)$$

Considering all the reactions producing CH_3 and CF_3 products, and applying the material balance relationship, (7), we have, $CO \equiv \frac{1}{2}CF_3H + \frac{1}{2}CH_4 + C_2F_6 + CF_3CH_3 + C_2H_6 + CF_2CH_2$ (from 4) $+ \frac{1}{2}CF_2CH_2$ (from 10 and 11). Interpolating the experimental results into this equation yields the material balance below. (All quantities are expressed in units of moles $ml^{-1} \times 10^9$; temp. 150°.)

$$5{\cdot}18 \equiv 4{\cdot}44 + 0{\cdot}11 + 0{\cdot}38 + 0{\cdot}25 + 0{\cdot}18 + 0{\cdot}11 + 0{\cdot}02 = 5{\cdot}49$$

Considering the experimental difficulties, good agreement is obtained.

The relative rate constant for radical exchange, k_6, can be measured relative to the rate constant for H abstraction by CF_3, k_{12}, from a knowledge of the rates of formation of the C_2H_6, CH_3CF_3, CH_2CF_2 (from 4), CH_4, and CF_3H. Thus,

$$\frac{R_{\text{exch}}}{R_{\text{abstr}}} = \frac{k_6[CF_3][SnMe_4]}{k_{12}[CF_3][SnMe_4]} = \frac{2R_{C_2H_6} + R_{CH_4} + R_{CF_3CH_3} + R_{CF_2CH_2} \text{ (from 8)}}{R_{CF_3H}}$$

Experimentally at 150°, $R_{C_2H_6} = 1{\cdot}5$, $R_{CH_4} = 1{\cdot}8$, $R_{CF_3CH_3} = 2{\cdot}1$, $R_{CF_2CH_2}$ (from 8) $= 0{\cdot}92$, $R_{CF_3H} = 74{\cdot}0$, (mole $ml^{-1}\ s^{-1} \times 10^{12}$) for the $CF_3 + SnMe_4$ system.

Thus $k_6/k_{12} = 0{\cdot}11$. We have measured k_{12} in an independent series of experiments, (unpublished), k_{12} (150°) $= 10^{11.7}\, e^{-7250/RT}$ ml $m^{-1}\ s^{-1}$, and hence, the exchange rate constant, $k_6 = 1 \times 10^7$ ml $m^{-1}\ s^{-1}$.

While full quantitative analysis was not possible in the CF_3 plus BMe_3, $SiMe_4$, $GeMe_4$ systems, we estimate from the amounts of CH_4 and C_2H_6 produced in these systems that the rates of the radical exchange reactions are in the order,

$$BMe_3 > SnMe_4 \gg GeMe_4 = SiMe_4.$$

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