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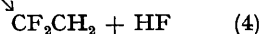
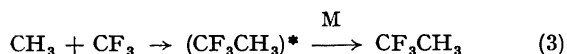
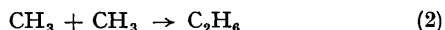
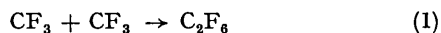
Radical Exchange in the Reaction of CF_3 Radicals with Organometallic Compounds

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Summary A radical exchange reaction occurs when CF_3 radicals react with some main-group organometallic compounds; for the system $\text{CF}_3 + \text{SnMe}_4$ $k_{\text{exch}} = 10^7 \text{ ml m}^{-1} \text{ s}^{-1}$.

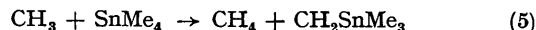
REBBERT and AUSLOOS¹ reported the exchange of methyl radicals in the system $\text{CH}_3 + \text{Hg}(\text{CH}_3)_2$. We have found that methane, ethane, and 1,1,1-trifluoroethane are formed in the reaction of CF_3 radicals with the methyls of B, Si, Ge, and Sn; this suggests that methyl radicals may be produced. If methyl radicals are formed, then the combination reactions (1), (2), and (3) would be expected to occur.



From (1), (2), and (3), $\Phi = R_{\text{CF}_3\text{CH}_3} / R_{\text{C}_2\text{H}_6} R_{\text{C}_2\text{F}_6}$.

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 $\text{CF}_3 - \text{SnMe}_4$. Thus at 150° , in the presence of 30 mm Hg of hexafluoroacetone (radical source), and 30 mm Hg of SnMe_4 , $R_{\text{CF}_3\text{CH}_3} = 2.1$, $R_{\text{C}_2\text{F}_6} = 3.2$, $R_{\text{C}_2\text{H}_6} = 1.5$, ($\text{mole ml}^{-1} \text{ s}^{-1} \times 10^{12}$). Thus experimentally $\Phi = 1.0$. 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).

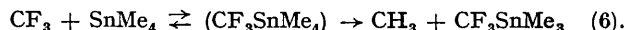
In the presence of SnMe_4 , we expect methyl radicals to produce methane by reaction (5).



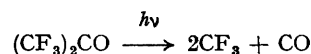
Thus $k_5 = R_{\text{CH}_4} \cdot k_2^{1/2} / R_{\text{C}_2\text{H}_6}^{1/2} [\text{SnMe}_4]$.

Experimentally at 150° using 30 mm Hg of hexafluoroacetone (radical source) and 30 mm Hg of SnMe_4 , we obtained $R_{\text{C}_2\text{H}_6} = 1.5 \times 10^{-12}$ and $R_{\text{CH}_4} = 1.8 \times 10^{-12}$ mole $\text{ml}^{-1} \text{ s}^{-1}$, thus yielding a value for $k_5 = 5.9 \times 10^6$ ml $\text{m}^{-1} \text{ s}^{-1}$. Gowenlock³ has independently measured k_5 (150°) = 5×10^6 ml $\text{m}^{-1} \text{ s}^{-1}$. We suggest the experimental evidence strongly supports the suggestion that the methyl products result from methyl radicals.

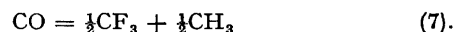
We have shown that methyl products are not obtained if SnMe_4 and hexafluoroacetone are heated, nor if SnMe_4 is photolysed under the experimental conditions. We suggest that methyl radicals are formed by a radical exchange process (6):



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

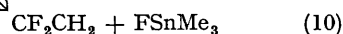
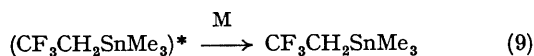
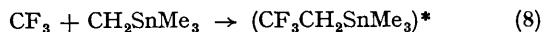


a material balance should hold, such that

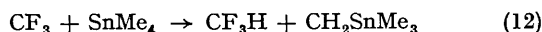


The volatile products of the reaction between CF_3 radicals and the organometallics are C_2F_6 , C_2H_6 , CF_3CH_3 , CF_2CH_2 , CH_4 , and CF_3H . The CF_2CH_2 is produced in (4); however, the pressure- and temperature-dependent characteristics of its formation, plus its formation in the dark

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 $\text{CF}_3 + \text{SnMe}_4$ we have (8), (9), (10), and (11).



From the data of Whittle³ on the $\text{CF}_3\text{CH}_3/\text{CF}_2\text{CH}_2$ 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)



Considering all the reactions producing CH_3 and CF_3 products, and applying the material balance relationship, (7), we have, $\text{CO} \equiv \frac{1}{2}\text{CF}_3\text{H} + \frac{1}{2}\text{CH}_4 + \text{C}_2\text{F}_6 + \text{CF}_3\text{CH}_3 + \text{C}_2\text{H}_6 + \text{CF}_2\text{CH}_2$ (from 4) + $\frac{1}{2}\text{CF}_2\text{CH}_2$ (from 10 and 11). Interpolating the experimental results into this equation yields the material balance below. (All quantities are expressed in units of moles $\text{ml}^{-1} \times 10^9$; temp. 150° .)

$$5.18 \equiv 4.44 + 0.11 + 0.38 + 0.25 + \\ 0.18 + 0.11 + 0.02 = 5.49$$

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,

$$\frac{R_{\text{exch}}}{R_{\text{abstr}}} = \frac{k_6[\text{CF}_3][\text{SnMe}_4]}{k_{12}[\text{CF}_3][\text{SnMe}_4]} = \\ \frac{2R_{\text{C}_2\text{H}_6} + R_{\text{CH}_4} + R_{\text{CF}_3\text{CH}_3} + R_{\text{CF}_2\text{CH}_2}}{R_{\text{CF}_3\text{H}}} \quad (\text{from 8})$$

Experimentally at 150° , $R_{\text{C}_2\text{H}_6} = 1.5$, $R_{\text{CH}_4} = 1.8$, $R_{\text{CF}_3\text{CH}_3} = 2.1$, $R_{\text{CF}_2\text{CH}_2}$ (from 8) = 0.92, $R_{\text{CF}_3\text{H}} = 74.0$, (mole $\text{ml}^{-1} \text{ s}^{-1} \times 10^{12}$) for the $\text{CF}_3 + \text{SnMe}_4$ system.

Thus $k_6/k_{12} = 0.11$. We have measured k_{12} in an independent series of experiments, (unpublished), $k_{12} (150^\circ) = 10^{11.7} e^{-7250/RT} \text{ ml m}^{-1} \text{ s}^{-1}$, and hence, the exchange rate constant, $k_6 = 1 \times 10^7 \text{ ml m}^{-1} \text{ s}^{-1}$.

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,



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³ A. U. Chaudrhy and B. G. Gowenlock, *J. Organometallic Chem.*, 1969, **16**, 221.

⁴ T. N. Bell and U. F. Zucker, *Canad. J. Chem.*, 1969, **47**, 1701.