The Gas Phase Displacement of $CF_3\cdot$ by $CH_3\cdot$ in $CF_3N_2CF_3$

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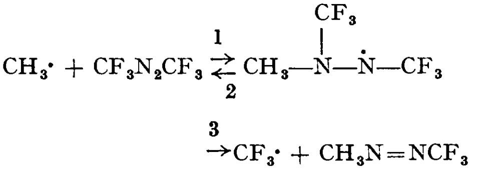
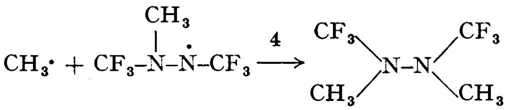
PITTS, TOLBERG, and MARTIN[1] have obtained evidence for the $CH_3\cdot$ displacement of $CH_3CO\cdot$ upon reaction of $CH_3\cdot$ with methyl *trans*-propenyl ketone in the gas phase. This presumably occurs *via* the addition of $CH_3\cdot$ across the C–C double bond. We report a similar displacement reaction *via* the addition of $CH_3\cdot$ across the N–N double bond of $CF_3N_2CF_3$ in the gas phase followed by the elimination of $CF_3\cdot$.



$$CH_3\cdot + CF_3N_2CF_3 \underset{2}{\overset{1}{\rightleftarrows}} CH_3—\overset{\overset{\displaystyle CF_3}{|}}{N}—\dot{N}—CF_3 \xrightarrow{3} CF_3\cdot + CH_3N{=}NCF_3$$

The addition process is exothermic to the extent of ~20 kcal./mole and therefore results in the production of an excited radical, the excess energy being initially located about the CH_3–N bond. For the displacement reaction to occur in addition to the reverse process 2, there must be a net "flow" of energy into the CF_3–N bond. The fact that this reaction occurs suggests that the CF_3–N bond energy is at most equal to the CH_3–N bond energy or, more likely, less than this value. If we generalise this statement for CH_3–C *versus* CF_3–C bond energies, this is in conflict with Szwarc *et al.*[2] and gives support for the lower bond energy cited for C_2F_6.[3]

Delocalisation of the excess energy in $CF_3–\underset{*}{\overset{\overset{\displaystyle CH_3}{|}}{N}}–\dot{N}–CF_3$ and collisional processes will produce a stable radical and we might expect the substituted hydrazine to be formed.



$$CH_3\cdot + CF_3–\overset{\overset{\displaystyle CH_3}{|}}{N}–\dot{N}–CF_3 \xrightarrow{4} (CF_3)(CH_3)N–N(CF_3)(CH_3)$$

Evidence for the displacement process is shown by the production of CF_3H and $CF_2{=}CH_2$ in the reaction of di-t-butyl peroxide (dtBP) with $CF_3N_2CF_3$ in the gas phase in the temperature range 140—170° using 8 mm. Hg of $CF_3N_2CF_3$ and 45 mm. Hg of dtBP. At these temperatures $CF_3N_2CF_3$ does not undergo thermal decomposition. $CF_3\cdot$ radicals from the displacement process abstract hydrogen from dtBP and acetone (produced from the decomposition of the

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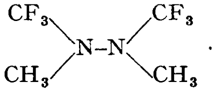
[1] J. N. Pitts, Jr., R. S. Tolberg, and T. W. Martin, *J. Amer. Chem. Soc.*, 1954, **76**, 2843.
[2] H. Komazawa, A. P. Stefani, and M. Szwarc, *J. Amer. Chem. Soc.*, 1963, **85**, 2043.
[3] E. Tschuikow-Roux, *J. Phys. Chem.*, 1965, **69**, 1075.

t-butoxy-radical) to give CF_3H, while $CF_2{=}CH_2$ is produced *via* the disproportionation reaction of $CF_3\cdot$ and $CH_3\cdot$.[4]

$$\begin{array}{ccc} CF_3\cdot + \text{dtBP} & \xrightarrow{5} & CF_3H + \text{dtPB}\cdot_{-\text{H}} \\ \text{or} & & \text{or} \\ (CH_3)_2CO & & CH_3COCH_2\cdot \end{array}$$

$$CF_3\cdot + CH_3\cdot \xrightarrow{6} CH_2{=}CF_2 + HF$$

There is no evidence as yet for CH_3CF_3, which should be present, or C_2F_6, which however should be produced in very small quantities because of the low steady-state concentration of $CF_3\cdot$. There is some, although not conclusive, evidence for the production of both $CF_3N_2CH_3$ and



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[4] W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, 1965, **61**, 244.