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The Addition of Sulphur Chloride Pentafluoride to Trifluoroethylene

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Summary The free radical addition of SF_5Cl to trifluoroethylene in the gas phase yields both adducts (a) SF_5-$CHFCF_2Cl$ and (b) SF_5CF_2CHFCl, the ratio [a]/[b] depending not only on temperature but also on the absolute concentration of SF_5Cl: these observations can be accounted for in terms of reversible addition of $\cdot SF_5$ radicals.

A recent paper describes both the photochemical and peroxide initiated addition of sulphur chloride pentafluoride to trifluoroethylene.[1] Both adducts [*i.e.* (a) SF_5CHFCF_2Cl and (b) SF_5CF_2CHFCl] were formed and the authors assume that the reaction involves an $SF_5\cdot$ chain as suggested previously.[2]

$$SF_5Cl \xrightarrow{h\nu} SF_5\cdot + Cl\cdot$$

$$SF_5\cdot + E \xrightarrow{k_2^a(k_2^b)} SF_5E\cdot \quad (E = \text{Trifluoroethylene})$$

$$Cl\cdot + E \xrightarrow{k_4} ClE\cdot$$

$$SF_5E\cdot + SF_5Cl \xrightarrow{k_3^a(k_3^b)} SF_5ECl + SF_5\cdot$$

$$ClE\cdot + SF_5Cl \xrightarrow{k_5} ECl_2 + SF_5\cdot$$

Different proportions of the two isomeric adducts (a) and (b) were formed in the photochemical [(a)/(b) = 2·7] and in the peroxide [(a)/(b) = 13] initiated experiments. For unstated reasons the authors[2] regard the ratio obtained in their photochemical reaction as abnormal and suggest that this is due to a displacement reaction of sulphur.

$$ECl\cdot + SF_5Cl \xrightarrow{?} SF_5ECl + Cl\cdot$$

This mechanism requires the additional assumption that the reactivity of the two isomeric radicals ($ECl\cdot$) either $CClF_2\dot{C}HF$ or $CClHF\dot{C}F_2$ is different. There are two objections to this argument. Firstly, as the authors themselves point out, no $SF_5CHFCF_2SF_5$ was isolated, although it would be expected in an exactly analogous reaction. Secondly, the halogen atoms are so tightly packed around the sulphur atom in sulphur chloride pentafluoride as to make a displacement reaction virtually impossible.

We have recently reported kinetic studies involving the addition of sulphur chloride pentafluoride to ethylene ($k_2^{C_2H_4} = 10^{5\cdot6}e^{-1900/RT}$ l mole^{-1} sec^{-1}).[3] This low activation energy might lead one to expect addition to an unsymmetric olefin would be very unselective. However, in our photochemical gas phase experiments involving trifluoroethylene we find the ratio (a)/(b) to vary from 11—36 depending not only on temperature but also on SF_5Cl concentration. The Table lists the averages from a series of runs (*ca.* 4 to each temperature) carried to about 5% conversion. The experimental method is described in ref. 3. It is clear that $[S_2F_{10}]_f/[ECl_2]_f$ is approximately unity, and in another set of experiments the yield of adduct was found to be proportional to the half power of the incident light intensity. These observations are consistent

The addition of SF_5Cl *to trifluoroethylene*

$[SF_5Cl]_i = 2\cdot78 \times 10^{-3}$ mole l^{-1}

$[CHF{=}CF_2]_i = 9\cdot27 \times 10^{-4}$ mole l^{-1}

Temp °	$[S_2F_{10}]/[ECl_2]_f$	$[a]_f/[ECl_2]_f$	$[a]_f/[b]_f$
63	1·13	0·617	23·7
92	1·07	0·392	19·4
123	1·09	0·372	14·1
160	1·08	0·284	10·9

with the suggested mechanism if the combination of $SF_5\cdot$ radicals is the principal chain termination step.

$$SF_5\cdot + SF_5\cdot \xrightarrow{k_6} S_2F_{10}$$

However to account for the high selectivity and the decrease in the $[a]_f/[ECl_2]_f$ ratio with temperature we must include the reverse of reaction 2 (see ref. 3).

$$SF_5E\cdot \xrightarrow{k_{-2}} SF_5\cdot + E$$

Application of the steady-state approximation to the overall mechanism leads to the following rate expression (initial rate):

$$\frac{\text{(Rate of formation of a)}}{\text{(Rate of formation of b)}} = \frac{k_2^a\,([SF_5Cl] + k^b_{-2}/k_3^b)}{k_2^b\,([SF_5Cl] + k^a_{-2}/k_3^a)}$$

This expression shows that the ratio of the products depends not only on k_2^a/k_2^b but also on the ratios k^b_{-2}/k_3^b and k^a_{-2}/k_3^a and the SF_5Cl concentration. By varying the concentration of SF_5Cl we have been able to measure k^a_{-2}/k_3^a from the ratio $[a]_f/[ECl_2]_f$ (see ref. 3). But because of the small amount of isomer (b) we have not been able to determine k^b_{-2}/k_3^b. However, results with other fluoro-olefins lead us to believe that $k^b_{-2}/k_3^b \gg k^a_{-2}/k_3^a$. In conformity with this we find an increase in $[SF_5Cl]_1$ decreases the ratio (a)/(b) and this probably partly explains the discrepancy between our photochemical results and the photochemical results of Haszeldine ***et al.*** in which the SF_5Cl concentration is much higher (their experiment is almost carried to completion, so that the instantaneous rate expression given above is only approximately correct in their case). It is difficult to predict the expected (a)/(b) ratio in the peroxide-initiated experiment of Haszeldine ***et al.*** Their SF_5Cl concentration is higher which should decrease the ratio, but the temperature is also higher and this would also decrease the ratio (*cf.* Table). There may, in addition, be a change in mechanism in this heterogeneous experiment (no 1,2-dichloro-1,1,2-trifluoroethane is reported and the yield of disulphur decafluoride is extremely small).

The reversible nature of thiyl radical addition is well known.[4] The present results emphasise that the relative orientation of radical addition to olefins when such reversible reactions occur depends not only on the nature of the reactants but also on their concentration.

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