INTRODUCTION

In 1950, trifluoromethyl and pentafluoroethyl radicals were produced by the photolysis of the corresponding iodides[20]. This led to an extensive investigation of the addition of $CF_3^\bullet$ radicals to unsaturated centres. Haszeldine and co-workers carried out a number of studies on the addition of CF_3 radicals to olefins[12]. The method applied by Haszeldine is discussed in Part (II) introduction and results are discussed in the general introduction. The work by Haszeldine was rather qualitative and no kinetic data were reported.

Szwarc, who was very active in this field, studied the kinetics of CF_3 radical addition to a number of unsaturated centres. The method applied is also discussed in Part (II) introduction as well as to the approach used to put the work on an absolute scale. Szwarc has interpreted his results in terms of the transition state theory. It was noticed that replacement of hydrogen atom by a methyl group or a chlorine at the site of addition decreases the Arrhenius pre-exponential term by a factor of five. This was explained in terms of a restricted rotation of the $CF_3^\bullet$ radical in the transition state. A reasonable correlation between the activation energies and ionisation potentials for a series of methyl-substituted olefins was obtained[21]. Szwarc also gave evidence for the strongly electrophilic character of the trifluoromethyl radicals[34]. A secondary deuterium effect study[35] led him to conclude that the incipient R-C bond (R=CF_3 or CH_3) is relatively long and that the configuration around the reactive centre remained unaltered (ie. planar) in the transition state.

The rate of addition of $CF_3^\bullet$, CCl_3, n-$C_3F_7^\bullet$ and n-$C_3F_7^\bullet$

radicals to ethylene was determined by Sangster and Thyne[22]. The rate and Arrhenius parameters were put on an absolute scale relative to those for hydrogen abstraction from hydrogen sulphide which were available. The difference in reactivity between the most reactive CF_3 radical and CCl_3 radical was almost entirely due to the variation of theactivation energy term.

The relative Arrhenius parameters for the addition of CF_3 radicals, produced from the photolysis of trifluoroiodomethane, to 1,1-difluoroethylene were obtained by Braslawsky, Casas and Cifuents[23]. Mercury was present in the system to trap the iodine atoms.

In 1973, Tedder and Walton[24] reported in a communication the results obtained for a study of the orientation of the gas phase addition of a series of $CF_3^{\cdot}$, $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$, n-$C_4F_9^{\cdot}$, n-$C_7F_{15}^{\cdot}$, n-$C_8F_{17}^{\cdot}$ and i-$C_3F_7^{\cdot}$ radicals to vinyl fluoride, 1,1-difluoroethylene and trifluoroethylene. A comparison of the orientation ratios for the addition of these radicals to different ends of the unsymmetrical fluoroolefins studied, showed a substantial increase in selectivity in the series $CF_3^{\cdot}$, $CF_3CF_2^{\cdot}$, $(CF_3)_2CF^{\cdot}$ radicals. On the other hand the difference in selectivity in the linear series $C_2F_5^{\cdot}$, n-$C_3F_7^{\cdot}$, n-$C_4F_9^{\cdot}$, n-$C_7F_{15}^{\cdot}$ and n-$C_8F_{17}^{\cdot}$ radicals was very small. This assumes that the steric interaction at the carbon carrying the unpaired electron is virtually the same with the linear series. It appeared then that the size and shape of the attacking radical is fairly important in the transition state, rather than electronic factors. This conclusion had to be confirmed. In order to attempt to determine the important role steric and other factors play in the addition of fluoroalkyl radicals to unsymmetrical olefins, a series of radicals $CF_3^\cdot$, $C_2F_5^\cdot$, i-$C_3F_7^\cdot$ and t-$C_4F_9^\cdot$ seemed to be very appropriate to study.

The addition of $CF_3^\cdot$ radicals has been discussed above. Tedder, Walton and co-workers[25, 26] determined the relative Arrhenius parameters for the addition of CF_3 radicals to fluoro-olefins and propene as well as a series of vinyl monomers[27]. Unlike most authors, their work was put on an absolute scale by comparing it to the addition to one end of ethylene of which the absolute parameters were determined. Also this present work was put on an absolute scale in the same way.

The addition of pentafluoroethyl radicals, the second in the linear as well as the branching series, to fluoro-olefins was only studied qualitatively. Haszeldine[28] studied the addition of C_2F_5 radicals to tetrafluoroethylene where a polymeric product of the form $C_2F_5(CF_2CF_2)_nI$ was obtained. Later the same author[12(f)] studied the direction of addition of C_2F_5 radicals to 1, 1-difluoroethylene. The addition was almost exclusively (90%) to the -CH_2 end. That was explained in terms of the stability of the intermediate fluoroalkyl radicals thus formed in the initial addition of C_2F_5 radical to the fluoroethylene. This was further confirmed by Chambers and his group[29] when studying telomerisation reactions in which C_2F_5 was used as a telogen. The same author showed that the strength of the C-I bond decreased sharply in the series $CF_3I > C_2F_5I >$ n-$C_3F_7 >$ i-C_3F_7I through an investigation of the exchange of labelled iodine and fluorocarbon iodides. The is less than for n-C_3F_7I (88%) the range of telomers produced with the former is considerably less, giving mainly 1:1 adduct. This led to the conclusion that C_2F_5I is a more efficient chain-transfer agent than n-C_3F_7I which is not consistent with the relative C-I bond strengths of the two iodides.

Apart from these qualitative studies there were no kinetic data reported for the addition of C_2F_5 radicals to unsaturated substrates. Tedder and Walton[30] reported the relative Arrhenius parameters for the gas phase addition of pentafluoroethyl (this work is described in Part (I) of this thesis) and perfluoro-t-butyl radicals to vinyl fluoride. The results showed that C_2F_5 radicals are more selective than CF_3 radicals and this difference in selectivity is mainly attributed to difference in activation energy parameters. Also the results showed that both radicals adds preferentially to the -CH_2 end of vinyl fluoride. The kinetic data for the addition of perfluoroisopropyl radicals to various fluorinated alkenes were reported by Tedder and Walton's group[31].

Pentafluoroethyl radicals were involved in some abstraction reactions amongst which Price and Kutschke[32] studied the reactions of C_2F_5 radical with hydrogen and methane. They found that the order of ease of hydrogen abstraction from a given substrate is $CF_3^\cdot > C_2F_5^\cdot > C_3F_7^\cdot > CH_3^\cdot$. This sequence of reactivity was measured according to the rate constants at 200°C. The radicals were produced by the photolysis of $(C_2F_5)_2CO$. Pritchard and Foote[33] also studied the reactions of $C_2F_5^\cdot$ and $C_3F_7^\cdot$ radical s with H_2 and D_2. They obtained a low activation energy for the reaction of $C_2F_5^\cdot$ radical with D_2.

The lack of kinetic studies for $C_2F_5^{\cdot}$ radical addition reactions left a gap in an important sequence in both increasing chain length in the linear series CF_3, n-C_3F_7, n-C_4F_9, and, branching in the series CF_3, i-C_3F_7, t-C_4F_9. This present work involves the kinetic study of $C_2F_5^{\cdot}$ radicals to vinyl fluoride, 1,1-difluoroethylene, trifluoroethylene and tetrafluoroethylene. Therefore this work filled the gap and could assist in obtaining a better understanding of the nature of the factors playing a role in these addition reactions. These reactions which appear to be quite important industrially in the production of fluorocarbon polymer systems.