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FREE RADICAL ADDITION TO OLEFINS. PART 23. THE ADDITION OF PENTAFLUOROETHYL RADICALS TO FLUORO-OLEFINS

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SUMMARY

Relative Arrhenius parameters have been determined for the addition of pentafluoroethyl radicals to each end of vinyl fluoride, vinylidene fluoride, trifluoroethylene and to tetrafluoroethylene taking ethylene as standard. The results compare very well with our earlier data for trifluoromethyl radicals. The pentafluoroethyl radicals are more selective and this selectivity can be attributed to changes in the activation energy term. The combined data are used to produce "revised" data for heptafluoropropyl radicals.

INTRODUCTION

In 1950 Professor H. J. Emeleus and coworkers described the photolysis of trifluoromethyl iodide [1]. The discovery that trifluoromethyl radicals could be readily prepared in this way led to extensive synthetic and mechanistic studies. In particular Haszeldine, one of the co-authors of the original paper, made an extensive study of the addition of trifluoromethyl radicals to olefins [3]. The present research has been concerned with putting a study of directive effects in free radical addition reactions on a firm quantitative basis [4]. In particular we have determined relative Arrhenius parameters for the addition of trifluoromethyl [5] and heptafluoropropyl radicals [6]. The latter is the considerably more selective radical of the two, and this greater selectivity goes with greater activation energy differences for addition to various sites. The purpose of the present investigation is to see if there is a general gradation from trifluoromethyl through pentafluoroethyl to heptafluoropropyl radicals in both selectivity and activation energy differences.

EXPERIMENTAL

The experiments were performed in a conventional vacuum line, with a "pyrex" reaction vessel (200 c. c.). The ratios of the products were estimated by gas chromatography using a gas density balance as detector. The products were identified by coupled gas chromatography/ mass spectroscopy. The reactions times varied from 3 hrs for the least reactive olefins (CH_2=CF_2) at low temperatures, to 1 min for the most reactive olefins (CH_2=CH_2 and CH_2=CHF) at high temperatures. The times were chosen to give ca. 5% conversion.

Vinyl Fluoride

A series of preliminary experiments were carried out in which mixtures of pentafluoroethyl iodide (60 mm) and vinyl fluoride (20 mm) were irradiated by a medium pressure mercury lamp. The two adducts ($C_2F_5CH_2CHFI$ and $C_2F_5CHFCH_2I$) had been identified previously. The series was then repeated with ethylene (20 mm) as well as vinyl fluoride. The results are tabulated below.

TABLE I

The Addition of Pentafluoroethyl Radicals to Ethylene and Vinyl Fluoride

10^3K/T	$\log \frac{[C_2F_5CH_2CHFI]}{[C_2F_5CH_2CH_2I]}$	$\log \frac{[C_2F_5CHFCH_2I]}{[C_2F_5CH_2CH_2I]}$
3.32	-0.323	-1.963
3.12	-0.287	-1.842
2.99	-0.251	-1.757
2.82	-0.268	-1.690
2.63	-0.225	-1.610
2.49	-0.225	-1.520
2.40	-0.208	-1.462
2.27	-0.172	-1.375
2.11	-0.128	-1.268

A least squares plot of log $[C_2F_5CH_2CHFI]$ against 10^3K/T gave a gradient of -0.14 and an intercept of 0.13, while a similar plot of log $[C_2F_5CHFCH_2I]/[C_2F_5CH_2CH_2I]$ gave a gradient of -0.55 and an intercept of -0.14.

Trifluoroethylene

A mixture of pentafluoroethyl iodide (80 mm) trifluoroethylene (20 mm) and ethylene (10 mm) was irradiated at 116° for 90 mins and the product analysed on g.l.c. coupled ms. The principle product peaks were $C_2F_5CHFCF_2I$ (m/e 328 P^+; 201, $C_4F_8H^+$; 177 CF_2I^+), $C_2F_5CF_2CHFI$ (m/e 328 P^+ ; 159 $CHFI^+$) and $C_2F_5CH_2CH_2I$ (m/e 274 P^+; 141 CH_2I^+) eluted in that order. The ion CF_2I^+ was present in the spectra of both the trifluoroethylene adducts, but $CHFI^+$ was only in the second isomer and CH_2I^+ in the spectrum of the ethylene adduct so that by taking note of the base peaks the evidence for their structure is unequivocal.

TABLE II

The Addition of Pentafluoroethyl Radicals to Ethylene and Trifluoroethylene

$10^3K/T$	$\log \frac{[C_2F_5CHFCF_2I]}{[C_2F_5CH_2CH_2I]}$	$\log \frac{[C_2F_5CF_2CHFI]}{[C_2F_5CH_2CH_2I]}$
3.26	-1.037	-1.764
3.13	-0.983	-1.651
3.04	-0.839	-1.490
2.93	-0.923	-1.549
2.77	-0.807	-1.403
2.68	-0.742	-1.329
2.54	-0.713	-1.206
2.40	-0.594	-1.118
2.24	-0.863	-1.268
2.13	-0.864	-1.210

A least squares plot of log $[C_2F_5CHFCF_2I]/[C_2F_5CH_2CH_2I]$ against $10^3K/T$ gave a gradient of -0.48 ± 0.06 and an intercept of 0.52 ± 0.16 while a similar plot of log $[C_2F_5CF_2CHFI]/[C_2F_5CH_2CH_2I]$ gave a gradient of -0.72 ± 0.06 and an intercept of 0.61 ± 0.16.

Tetrafluoroethylene

The photolysis of a mixture of pentafluoroethyl iodide (80 mm), tetrafluoroethylene (30 mm) and ethylene (15 mm) gave besides the expected adducts, telomers the first of which was produced in sufficient yield to affect the results. The first adduct peak to be eluted was C_4F_9I (m/e = 346, P^+; 219, $C_4F_9^+$; 177, CF_2I^+) followed by $C_2F_5CH_2CH_2I$ (m/e = 274, P^+; $CH_2CH_2I^+$, 155; CH_2I^+, 141) and then by the major telomer $C_4F_9CH_2CH_2I$ (m/e = 378, P^+; $CH_2CH_2I^+$, 155; CH_2I^+, 141).

TABLE III

The addition of Pentafluoroethyl Radicals to Ethylene and Tetrafluoroethylene

10^3K/T	log $\frac{([C_4F_9CH_2CH_2I] + [C_4F_9I]}{[C_2F_5CH_2CH_2I]}$
3.27	-0.909
3.10	-0.783
3.04	-0.766
2.99	-0.757
2.82	-0.641
2.70	-0.706
2.67	-0.627
2.58	-0.644
2.54	-0.621
2.47	-0.586
2.41	-0.595
2.27	-0.495

A least squares plot of log ($[C_4F_9CH_2CH_2I] + [C_4F_9I]/[C_2F_5CH_2CH_2I]$) against 10^3K/T gave a slope of -0.33 ± 0.03 and an intercept of 0.23 ± 0.09.

Vinylidene Fluoride

A mixture of pentafluoroethyl iodide (40 mm) and vinylidene fluoride (20 mm) was photolysed and the two adducts distinguished by their mass spectra $C_2F_5CH_2CF_2I$ (m/e = 310 P^+; 177, CF_2I^+) and $C_2F_5CF_2CH_2I$ (m/e = 310 P^+; 141, CH_2I^+). There was a trace of telomer, but too little to affect the kinetic series.

TABLE IV

The Addition of Pentafluoroethyl Radical to Vinylidene Fluoride

10^3K/T	log $[C_2F_5CH_2CF_2I]/[C_2F_5CF_2CH_2I]$
2.04	-1.682
2.11	-1.757
2.20	-1.863
2.31	-1.917
2.52	-2.087
2.61	-2.056
2.70	-2.215
2.75	-2.153
2.77	-2.161
3.00	-2.216
3.24	-2.783

A least squares plot of $\log[C_2F_5CH_2CF_2I]/[C_2F_5CF_2CH_2I]$ against 10^3K/T gave a slope of -0.56 ± 0.04 and an intercept of -0.59 ± 0.09.

The reaction of vinylidene fluoride was also studied competitively with tetrafluoroethylene. Telomers were produced and identified by their mass spectra:- $C_6F_{13}I$; $C_2F_5CH_2(CF_2)_3I$; $C_4F_9CH_2CF_2I$ and at high temperatures $C_8F_{17}I$.

TABLE V

The Addition of Pentafluoroethyl Radicals to Tetrafluoroethylene and Vinylidene Fluoride

10^3K/T	$\log \dfrac{([C_4F_9I] + [C_6F_{13}I] + [C_4F_9CH_2CF_2I] + [C_8F_{17}I])}{([C_2F_5CH_2CF_2I] + [C_2F_5CH_2CF_2CF_2CF_2I])}$
2.06	-0.028
2.19	-0.009
2.31	-0.016
2.43	-0.027
2.60	-0.033
2.65	-0.082
2.80	-0.073
2.99	-0.141
3.24	-0.161

A least squares plot of the logarithm of the product ratio (corrected for the ratio of the starting olefins) against 10^3K/T gave a gradient of -0.16 ± 0.02 and an intercept of 0.35 ± 0.05.

As a further cross check the reaction with vinylidene fluoride was run competitively with ethylene. In a series of runs pentafluoroethyl iodide (60 mm) was photolysed in the presence of vinylidene fluoride (25 mm) and ethylene (15 mm). The three adducts were eluted in the order $C_2F_5CH_2CF_2I$, $C_3F_7CH_2I$ and $C_2F_5CH_2CH_2I$ and this was confirmed by coupled g. l. c. /m. s. analysis.

TABLE VI

The Addition of Pentafluoroethyl Radicals, to Vinylidene Fluoride and Ethylene

10^3K/T	log ([$C_2F_5CH_2CF_2I$]/[$C_2F_5CH_2CH_2I$])
2.09	-0.487
2.29	-0.504
2.49	-0.560
2.60	-0.576
2.73	-0.628
2.91	-0.696
3.00	-0.676
3.25	-0.783

A least squares plot of the logarithm of the product ratio (corrected for the proportions of the starting olefins) against 10^3K/T gave a slope of -0.26 ± 0.02 and an intercept of 0.07 ± 0.06.

DISCUSSION

Table VII shows the orientation of addition of pentafluoroethyl radicals to the unsymmetrical fluoroethylenes. Also included are our earlier results for trifluoromethyl [5] and n-heptafluoropropyl radicals [6].

TABLE VII.

The Orientation α/β of the Addition of Trifluoromethyl, Pentafluoroethyl and n-Heptafluoropropyl Radicals to Fluoroethylenes at 164°C

Olefin α β	Radical $CF_3\cdot$ [5]	$C_2F_5\cdot$ [a]	n-$C_3F_7\cdot$ [6]
$CHF=CF_2$	2.0	2.9	4.0
$CH_2=CHF$	10.6	16.4	20.0
$CH_2=CF_2$	31.3	76.9	111.0

[a] Present work

It is immediately apparent that there is a gradual increase in the selectivity of the three radicals as the number of carbon atoms increases, and present results confirm quantitatively our earlier work in which the orientation of addition of a number of perfluoroalkyl radicals were studied [7].

Table VIII shows the relative Arrhenius parameters for the addition of trifluoromethyl and pentafluoroethyl radicals (taking ethylene as standard). The important feature to notice about the Table VIII is that the observed changes in selectivity between the radicals are due to greater differences in the activation energy terms for pentafluoroethyl radicals. The ratios of the pre-exponential terms (A/A_e) are usually less than one. The table also includes a column derived from our earlier work with n-heptafluoropropyl radicals. This latter work was carried out before we had perfected our technique and, more important, each olefin was not run competitively with ethylene. This means that the original values of A/A_e and ($E-E_e$) are the results of ratios of ratios. Table VIII shows that the actual orientation ratios form a very consistent pattern and it seems probable that the actual relative rates in the original heptafluoropropyl radical study were correct but that the scatter of points in the Arrhenius plots were sufficient to give poor intercepts. We have therefore calculated "revised" Arrhenius parameters, assuming that the product ratios determined at 164° were correct but taking assumed values for log (A/A_e) which represent an average of the ratio (A/A_e) for trifluoromethyl radicals [5] and heptafluoro-2-propyl radicals [8]. We have calculated "revised" Arrhenius parameters whenever the original value of log (A/A_e) was

TABLE VIII.

Relative Arrhenius Parameters for the Addition of Trifluoromethyl, Pentafluoroethyl and n-Heptafluoropropyl Radicals to Fluoroethylenes

Olefin	Radical					
	$CF_3\cdot$ [a]		$C_2F_5\cdot$ [b]		$\underline{n}$-$C_3F_7\cdot$ [c]	
	log A/A_e	$(E-E_e)$	log A/A_e	$(E-E_e)$	log A/A_e	$(E-E_e)$
CH_2=CHF	-0. 1	+0. 5	0. 05	+0. 6	-0. 1	+0. 8
CH_2=CF_2	-0. 2	+1. 2	+0. 4	+1. 2	(-0. 1)	(+1. 7)
CHF=CH_2	-0. 3	+1. 9	-0. 2	+2. 5	+0. 1	+3. 2
CHF=CF_2	-0. 6	+1. 9	-0. 1	+2. 2	+0. 2	+3. 1
CF_2=CH_2	-0. 6	+3. 2	-0. 2	+3. 7	(-0. 3)	(+5. 4)
CF_2=CHF	-0. 5	+2. 7	-0. 0	+3. 3	+0. 2	+4. 1
CF_2=CF_2	-0. 1	+1. 7	+0. 2	+1. 5	(-0. 3)	(+2. 1)

E in k cal mol^{-1} Subscript e for Ethylene

[a] J. N. Cape, A. C. Greig, J. M. Tedder and J. C. Walton, J. C. S. Faraday I, 1975, 71, 592.

[b] Present Work.

[c] J. M. Tedder, J. C. Walton and K. D. R. Winton, J. C. S. Faraday I, 1972, 68, 160 [figures in brackets reclaculated].

greater than +0. 5; the "revised" values are shown in brackets. Recalculation of this kind can be justified by the very extensive data we now have and by the fact that the limited experimental data fit well with the "revised" Arrhenius parameters. Compared with our more recent studies there were just too few competitive experiments in the original work to get good Arrhenius parameters.

Figure 1 shows the activation energy differences $(E-E_e)$ plotted against each other. The values for the present work with pentafluoroethyl radicals are plotted along the horizontal axis and the corresponding values (i. e. for attack at the same sites) for trifluoromethyl and heptafluoropropyl ("revised") are plotted along the vertical axis. The present results show a linear relationship with both previous sets of data. The steeper slope

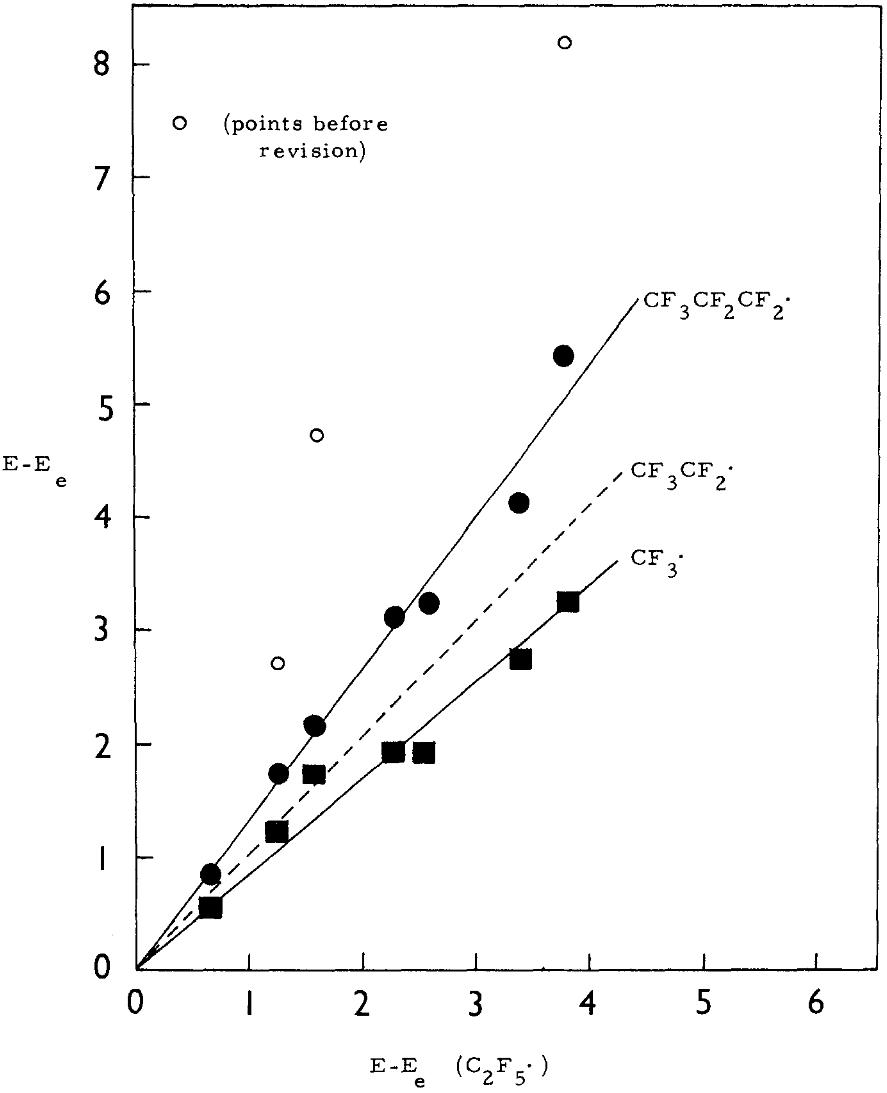

Figure I

as the radical becomes larger provides a quantitative measure of its increased selectivity. The figure also provides very good confirmation of the validity of the "revised" values for heptafluoropropyl radicals.

The present data fill in an important gap in kinetic data of radical addition reactions. We now have good data for the increasing branching series of radicals $CF_3\cdot$ [5], $CF_2CF_2\cdot$; $(CH_3)_2CF\cdot$ [8] and $(CF_3)_3C\cdot$ [9] and for the linear series $CF_3\cdot$ [5]; $CF_3CF_2\cdot$; $CF_3CF_2CF_2\cdot$ [7] (with qualitative data for $CF_3CF_2CF_2CF_2\cdot$ and for $CF_2(CF_2)_6\cdot$). This represents the most complete set of kinetic data where structure has been varied in a regular manner (eight different olefin sites and five different fluoroalkyl radicals).

REFERENCES

1 J. Banus, H. J. Emeleus, and R. N. Haszeldine; J. Chem. Soc., (1950) 3041.

2 Part 22, H. C. Low, J. M. Tedder and J. C. Walton, Int. J. Chem. Kinetics, 9 (1977) in the press.

3 R. N. Haszeldine, J. Chem. Soc. , (1952) 2504; R. N. Haszeldine and B. R. Steele, ibid. , (1953) 1199; R. N. Haszeldine, ibid. , (1953) 3565; R. N. Haszeldine and B. R. Steele, ibid. , (1954) 923; R. N. Haszeldine and B. R. Steele, ibid. (1957) 2193; 2800.

4 J. M. Tedder and J. C. Walton, Acc. Chem. Research. , 9 (1976) 183.

5 J. N. Cape, A. C. Greig, J. M. Tedder and J. C. Walton, J. Chem. Soc. Faraday I, 71 (1975) 592.

6 J. M. Tedder, J. C. Walton and K. D. R. Winton, J. Chem. Soc. Faraday I, 68 (1972) 160.

7 D. S. Ashton, A. F. Mackay, J. M. Tedder, D. C. Tipney and J. C. Walton, J. Chem. Soc. Chem. Commun. , (1973) 496.

8 L. L. T. Vertommen, J. M. Tedder and J. C. Walton, J. Chem. Research(S), (1977), 18-19.

9 L. L. T. Vertommen, J. M. Tedder and J. C. Walton, unpublished work.