Free Radical Substitution in Aliphatic Compounds. Part 32.[1] The Reaction of Trifluoromethyl Radicals with Butane, 1-Fluorobutane, and 1,1,1-Trifluoropentane

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Trifluoroiodomethane has been photolysed in the presence of butane, 1-fluorobutane, and 1,1,1-trifluorobutane in the gas phase. Using literature data for the attack of trifluoromethyl radicals on butane, Arrhenius parameters have been determined for the attack of trifluoromethyl radicals at each site in the substituted butanes. In an attempt to obtain similar data for methyl radicals, azomethane was photolysed in the presence of excess of methyl iodide. Although qualitative data concerning the attack of 1-substituted butanes by methyl radicals were obtained it was not possible to obtain good quantitative data by this technique.

ALTHOUGH there is ample data concerning the abstraction of hydrogen from alkanes by trifluoromethyl radicals [2-9] there is less information about hydrogen abstraction from substituted alkanes. Most of the important work in this field comes from Whittle and his co-workers and deals with halogen substituted methanes and ethanes.[10,11] There is very little data on how substituents affect attack by trifluoromethyl radicals further down the chain. The present research was intended to extend our studies of the effect substituents have on hydrogen abstraction from terminally substituted butanes (see previous Parts).

EXPERIMENTAL

The reactions were performed in a conventional vacuum line; the reaction vessel was Pyrex (310 ml), the light source a Hanovia UVS 220 medium pressure mercury arc, and the light passed through two Pyrex filters (1/16 in thick) in addition to the walls of the reaction vessel. The products of the reaction were analysed by g.l.c. using a 20% (w/w) silicone oil on 60—80 mesh Embacel packing and a gas density balance as detector. The order of elution of the fluoroiodobutanes and trifluoroiodopentanes could be determined by analogy with related compounds. We have previously studied the chlorination and bromination of fluorobutane and 1,1,1-trifluoropentane, and have found that the products are invariably eluted in the order

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$(X\overset{\alpha}{C}H_2{-}\overset{\beta}{C}H_2{-}\overset{\gamma}{C}H_2{-}\overset{\delta}{C}H_3)$ α, β, γ, δ. In the present study this order was confirmed by mass spectral analysis using coupled g.l.c.–m.s. Thus in the products derived from fluorobutane the one believed to be 1-fluoro-1-iodobutane had *m/e* 159 ($CHFI^+$) in its mass spectrum, a peak which was missing in the spectra of the other isomers, all of which had *m/e* 141 (CH_2I^+) not present in the first isomer. Similarly the second isomer eluted had *m/e* 173 ($C_2H_3FI^+$) not present in the third and fourth isomers. On the other hand the fourth isomer had *m/e* 156 ($C_2H_5I^+$) not present in any of the other spectra. All the isomers gave the correct molecular ion at *m/e* 252. Similar arguments could be applied to the products from 1,1,1-trifluoropentane except for the α-isomer which was present in too small yield for mass spectral analysis.

Trifluoromethyl Radicals and n-Butane.—Two series of experiments were carried out: Series A employed trifluoromethyl iodide (100 mmHg), butane (10 mmHg), and an irradiation time of 3 h, Series B employed equal pressures of trifluoromethyl iodide and butane (60 mmHg) and much shorter reaction times (10—15 min), but more important in Series B a small pool of mercury was present in the reaction vessel.

TABLE 1

n-Butane and trifluoromethyl radicals

Series A		Series B	
t/°C	$2[Bu^nI]/3[Bu^sI]$	t/°C	$2[Bu^nI]/3[Bu^sI]$
76 (3)	0.13	28 (7)	0.056
91 (4)	0.13	50 (6)	0.058
107 (8)	0.14	53 (2)	0.059
120 (7)	0.15	62.5 (3)	0.063
126 (2)	0.15	64 (9)	0.060
155 (1)	0.17	64.5 (8)	0.064
166 (6)	0.16	77.5 (4)	0.067
190 (5)	0.20	87 (5)	0.071
		100.5 (1)	0.078

Figures in parentheses indicate the number of analytical runs. Both series gave reasonable Arrhenius plots (log $2[Bu^nI]/3[Bu^sI]$ *versus* $10^3\ T^{-1}/K^{-1}$); the least squares values (taking individual analytical runs) were, Series A, gradient −0.26 ± 0.09, intercept −0.16 ± 0.04; Series B, gradient −0.23 ± 0.08, intercept −0.51 ± 0.03.

TABLE 2

1-Fluorobutane and trifluoromethyl radicals

t/°C	$\frac{[1\text{-F},1\text{-IC}_4H_8]}{[1\text{-F},3\text{-IC}_4H_8]}$	$\frac{[1\text{-F},2\text{-IC}_4H_8]}{[1\text{-F},3\text{-IC}_4H_8]}$	$\frac{2[1\text{-F},4\text{-IC}_4H_8]}{3[1\text{-F},3\text{-IC}_4H_8]}$
30	0.15	0.21	(6)
49.5	0.16	0.20	0.800 (7)
56	0.17	0.22	0.082 (5)
76	0.18	0.22	0.081 (4)
88	0.18	0.20	0.087 (2)
99	0.18	0.20	0.090 (1)
119			0.097 (8)
144			0.113 (9)

Figures in parentheses indicate the number of analytical runs. Arrhenius plots of $\log[1\text{-F},1\text{-IC}_4H_8]/[1\text{-F},3\text{-IC}_4H_8]$ against $10^3T^{-1}/K^{-1}$ gave least squares values of −0.14 ± 0.09 for the gradient and −0.36 ± 0.03 for the intercept; $\log[1\text{-F}, 2\text{-IC}_4H_8]/[1\text{-F}, 3\text{-IC}_4H_8]$ against $10^3\ T^{-1}/K^{-1}$ gave a gradient of +0.017 ± 0.012 and an intercept of −0.73 ± 0.04; $\log 2[1\text{-F}, 4\text{-IC}_4H_8]/3[1\text{-F}, 3\text{-IC}_4H_8]$ against $10^3\ T^{-1}/K^{-1}$ gave a gradient of −0.21 ± 0.08.

Trifluoromethyl Radicals and 1-Fluorobutane.—The reactions were carried out with mercury present in the reaction vessel; trifluoromethyl iodide (50 mmHg) and 1-fluorobutane (50 mmHg) were photolysed for 10 min.

Trifluoromethyl Radicals and 1,1,1-*Trifluoropentane.*—The reactions were carried out with mercury present in the reaction vessel; trifluoromethyl iodide (60 mmHg) and 1,1,1-trifluoropentane (60 mmHg) were photolysed for 10 min.

TABLE 3

1,1,1-Trifluoropentane and trifluoromethyl radicals

t/°C	$\frac{[1,1,1\text{-F}_3,2\text{-IC}_5H_8]}{[1,1,1\text{-F}_3,4\text{-IC}_5H_8]}$	$\frac{[1,1,1\text{-F}_3,3\text{-IC}_5H_8]}{[1,1,1\text{-F}_3,4\text{-IC}_5H_8]}$	$\frac{2[1,1,1\text{-F}_3,5\text{-IC}_5H_8]}{3[1,1,1\text{-F}_3,4\text{-IC}_5H_8]}$
75		0.20	0.084 (7)
88		0.21	0.091 (3)
112.5	0.0096	0.25	0.099 (2)
122	0.0106	0.26	0.099 (1)
148.5	0.0069	0.27	0.11 (4)
171	0.0085	0.30	0.13 (5)
198.5	0.0074	0.33	0.14 (6)

Figures in parentheses indicate the number of analytical runs. Arrhenius plots of $\log[1,1,1\text{-F}_3,2\text{-IC}_5H_8]/[1,1,1\text{-F}_3,4\text{-IC}_5H_8]$ against $10^3\ T^{-1}/K^{-1}$ gave least squares values of 0.28 ± 0.39 for the gradient and −2.73 ± 0.16 for the intercept; $\log[1,1,1\text{-F}_3,3\text{-IC}_5H_8]/[1,1,1\text{-F}_3,4\text{-IC}_5H_6]$ against $10_3T^{-1}/K^{-1}$ gave a gradient of −0.29 ± 0.04 and an intercept of +0.14 ± 0.01; $\log 2[1,1,1\text{-F}_3,5\text{-IC}_5H_8]/3[1,1,1\text{-F}_3,4\text{-IC}_5H_8]$ against $10^3T^{-1}/K^{-1}$ gave a gradient of −0.29 ± 0.04 and an intercept of −0.26 ± 0.02.

TABLE 4

1-Fluorobutane and methyl radicals

	Series A		
t/°C	$\frac{[1\text{-F},1\text{-IC}_4H_8]}{[1\text{-F},3\text{-IC}_4H_8]}$	$\frac{[1\text{-F},2\text{-IC}_4H_5]}{[1\text{-F},3\text{-IC}_4H_5]}$	$\frac{2[1\text{-F},4\text{-IC}_4H_8]}{3[1\text{-F},3\text{-IC}_4H_8]}$
85	0.86	1.20	0.38 (7)
95	0.90	1.16	0.30 (6)
116	0.85	1.14	0.36 (5)
135	0.86	1.17	0.34 (4)
146	0.93	1.07	0.34 (1)
182	0.86	1.08	0.33 (2)
208	0.81	0.98	0.29 (3)
	Series B		
118	1.04	1.15	0.17 (2)
134	0.97	1.14	0.18 (3)
161	0.90	0.97	0.19 (5)
166	0.84	0.89	(4)
188	0.80	0.74	0.21 (1)

Figures in parentheses indicate the number of analytical runs

TABLE 5

1,1,1-Trifluoropentane and methyl radicals

t/°C	$\frac{[1,1,1\text{-F}_3,2\text{-IC}_5H_8]}{[1,1,1\text{-F}_3,4\text{-IC}_5H_8]}$	$\frac{[1,1,1\text{-F}_3,3\text{-IC}_5H_8]}{[1,1,1\text{-F}_3,4\text{-IC}_5H_8]}$	$\frac{2[1,1,1\text{-F}_3,5\text{-IC}_5H_8]}{3[1,1,1\text{-F}_3,4\text{-IC}_5H_8]}$
153	0.27	0.42	0.27 (1)
177	0.22	0.41	0.26 (3)
192	0.27	0.37	0.22 (2)
211	0.33	0.44	0.23 (5)
240	0.28	0.46	0.23 (4)

Figures in parentheses represent analytical runs

Methyl Radicals and 1-*Fluorobutane.*—The reaction vessel was charged with azomethane (2 mmHg), methyl iodide (50 mmHg), and 1-fluorobutane (180 mmHg), and then irradiated for 3 h (Series A). In a second series of experiments (Series B), the proportions of the reactants were azomethane (2 mmHg), methyl iodide (180 mmHg), and 1-fluorobutane (180 mmHg). The irradiation time in Series B was varied from 2 to 3 h.

Methyl Radicals and 1,1,1-*Trifluoropentane.*—Mixtures of azomethane (3 mmHg), methyl iodide (180 mmHg), and 1,1,1-trifluoropentane (180 mmHg) were photolysed for periods from 2 to 3 h.

DISCUSSION

The trifluoromethyl radical data (Tables 1—3) for the reaction with butane show the expected trends with changing temperature, and the results in the presence of mercury are consistent with the chain reactions (1)—(3).[4,9] When no mercury was present the chains were

$$CF_3I \xrightarrow{h\nu} CF_3\cdot + I\cdot \qquad (1)$$

$$CF_3\cdot + RH \longrightarrow CF_3H + R\cdot \qquad (2)$$

$$R\cdot + CF_3I \longrightarrow RI + CF_3\cdot \qquad (3)$$

very much shorter and termination in iodine must have been an important process. The chain length is important since the initiation step is almost certain to yield thermally excited trifluoromethyl radicals and electronically excited iodine atoms, so that ratios of products obtained from short chain reactions would not necessarily reflect the reactivity of the trifluoromethyl radical in its ground state. The marked difference between the reaction times and the temperature coefficients for the experiments with and without mercury shows that chain length does affect the results. The reactions without mercury required much longer reaction times, were much less selective, and gave a very much smaller temperature coefficient. These differences are all consistent with the presence of short chains and participation by excited species. In our view therefore experiments carried out using a full mercury arc, long reaction times (and short reaction chains, *i.e.* <20) and no mercury to trap the iodine formed,[4] must be treated with some reserve even though the results fit in well with other work.

The more recent work of Whytock and his co-workers uses filtered light but the chains are still not very long and unfortunately neither the relative proportions of the reactants nor their absolute pressure are reported.[9] However, the temperature coefficients reported by these authors indicate that participation by excited species was unimportant. In fact the relative Arrhenius parameters reported by Whytock and his co-workers show an activation energy difference considerably greater than that determined in the present study. The relative selectivities at 90 °C are RS_p^s 7.6 (present work, no mercury present), 14.0 (present work, mercury present), and 13.0 (Whytock *et al.*). At this temperature our results and Whytock's are in good agreement but they diverge at higher temperatures leading to equation (4) for the present work and (5) for Whytock

$$\log k_p/k_s = -0.51 - (1\,050 \text{ cal mol}^{-1})/2.303RT \qquad (4)$$

$$\log k_p/k_s = +0.21 - (2\,633 \text{ cal mol}^{-1})/2.303RT \qquad (5)$$

and his co-workers. Their temperature range was 160—270 °C but we have found that the butyl iodides start to decompose (eliminate hydrogen iodide) at temperatures >190 °C and this may explain the discrepancy, although there is little evidence for curvature in Whytock's results. Possibly a combination of short chains at low temperatures and decomposition of the products at high temperatures has led to a mutual compensation of errors.

The reaction of trifluoromethyl radicals with 1-fluorobutane and 1,1,1-trifluorobutane has not been investigated before. Examination of the results shows that the ratios [1-fluoro-4-iodobutane]/[1-fluoro-3-iodobutane] from the reactions with fluorobutane are almost identical to the ratios [1,1,1-trifluoro-5-iodopentane]/[1,1,1-trifluoro-4-iodopentane] from the reactions with trifluoropentane at the same temperature. This is in accord with all our previous experience of free radical substitution in the gas phase.[12] The almost complete identity of the two series of results confirms the reliability of the experimental method for the γ- and δ-positions. Similarly the data for the β-position, though different for the two fluoroalkanes looks reasonable. However the rate of attack at the α-position in 1,1,1-trifluoropentane is so small (and in the chromatogram the peaks for the α- and β-iodo-compounds slightly overlap) that the figures cannot be used to estimate Arrhenius parameters. Instead, in Table 6, we have assumed a pre-exponential factor of 8.0 l mol^{-1} s^{-1} and calculated the corresponding activation energy assuming the ratio at 150 °C is correct. The absolute rate for attack at the γ-position (k_γ $2.5 \times 10^8 \exp - 5\,600/RT$) was taken by averaging the data in the literature.[2-5] The literature values refer to the whole molecule, so that the activation energy may be slightly overestimated. The pre-exponential factor has been chosen assuming the major part of the attack in n-butane is on the four secondary hydrogen atoms, so that per hydrogen attack at the γ-position in a substituted butane is exactly half this value. The experimental pre-exponential factors for $CF_3\cdot$ radicals and substituted butanes appear to be slightly low, more especially when compared with the trichloromethyl radical data. However the latter

TABLE 6

Arrhenius parameters for attack by trifluoromethyl and trichloromethyl radicals [13] on butane, 1-fluorobutane, and 1,1,1-trifluoropentane

X	CH_2		CH_2		CH_2		CH_3	
	α		β		γ		δ	
	log *A*	*E*	log *A*	*E*	log *A*	*E*	log *A*	*E*
				$CF_3\cdot$ Radicals				
H	7.9	6.6	8.4	5.6	*8.4*	*5.6*	7.9	6.6
F	8.1	6.2	7.7	5.5	*8.4*	*5.6*	8.0	6.5
CF_3	(8.0)	(11.4)	8.6	6.9	*8.4*	*5.6*	8.2	6.9
				$CCl_3\cdot$ Radicals				
H	9.0	14.3	8.8	10.7	*8.8*	*10.7*	9.0	14.3
F	9.1	12.6			*8.8*	*10.7*	9.4	14.5
CF_3	(9.0)	(14.0)	9.0	12.3	*8.8*	*10.7*	9.2	14.8

Figures in parentheses based on experiments at one temperature. The parameters for the γ-position are assumed. log *A* per H atom in l mol^{-1} s^{-1}, *E* is kcal mol^{-1}.

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values depend on the recombination rate for trichloromethyl radicals which is still open to some uncertainty.[14]

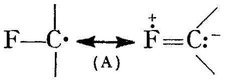
Table 6 convincingly shows that the α-substituent has no effect on attack by either trihalogenoalkyl radical at the γ- and δ-positions. The β-position in 1,1,1-trifluoropentane is deactivated to attack by both radicals but the single fluorine atom appears to have little effect. The α-position in 1-fluorobutane is, in comparison with the other terminal position, activated to attack by both radicals through a drop in the activation energy. This effect is usually attributed to weakening of the C–H bond by resonance stabilisation (A) of the incipient radical; this bond strength effect outweighing an opposing polar effect.[15] The α-position in trifluoropentane is very deactivated to both radicals, the effect being much more marked for trifluoromethyl radicals. However, it must be remembered that the Arrhenius parameters for both radicals at the α-position are derived from data at a single temperature.

TABLE 7

Effect of F and CF_3 as α-substituents in hydrogen abstraction by trifluoromethyl radicals [11]

	log A	E		log A	E		log A	E
$H–\overset{*}{C}H_3$	8.5	11.2	$H–\overset{*}{C}H_2CH_3$	8.2	8.3	$H–\overset{*}{C}H_2C_3H_7$	7.9	6.6
$F–\overset{*}{C}H_3$	8.6	11.2	$F–\overset{*}{C}H_2CH_3$	8.7	8.2	$F–\overset{*}{C}H_2C_3H_7$	8.1	6.2
$CF_3–\overset{*}{C}H_3$	8.7	13.5				$CF_3–\overset{*}{C}H_2C_3H_7$	8.0	11.4

log A per H atom in l mol^{-1} s^{-1}, E in kcal mol^{-1}.



(A)

Table 7 compares the observed effect of a fluorine atom and a trifluoromethyl group as α-substituents in methane, ethane, and butane. The trends are remarkably similar, the single fluorine atom having a negligible effect (compared to hydrogen) in each case. The trifluoromethyl group on the other hand clearly has a very marked deactivating effect, even though the accuracy of the ' butane ' figures is uncertain.

Table 4 shows that the methyl radical data cannot be used for determining relative Arrhenius parameters. The hoped for sequence was (6)—(10).[16] No products

$$(CH_3N)_2 \xrightarrow{h\nu} 2CH_3\cdot + N_2 \quad (6)$$

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot \quad (7)$$

$$CH_3\cdot + R^1H \longrightarrow CH_4 + R^{1}\cdot \quad (8)$$

$$R\cdot + CH_3I \rightleftharpoons RI + CH_3\cdot \quad (9)$$

$$R^{1}\cdot + CH_3I \rightleftharpoons R^1I + CH_3\cdot \quad (10)$$

arising from combination or disproportionation were observed, so it was hoped that by having sufficient methyl iodide the two equilibrium steps could be pushed over to the right. However the fact that increasing the proportion of methyl iodide had a significant effect on the γ : δ ratio shows that the required conditions had not been achieved.[16] Nonetheless the data probably give a correct picture of the relative selectivities, and we have therefore compared the relative selectivities of methyl, trichloromethyl, and trifluoromethyl radicals in Table 8. Methyl radicals show the same pattern of selectivity towards 1-fluorobutane as the two trihalogenomethyl radicals, except that the α-position is now very reactive compared with the δ. In trifluoropentane however, the α-position, which is strongly deactivated to the trihalogenomethyl radicals, is slightly activated to methyl radicals. Since we would expect the C–H bonds adjacent to a trifluoromethyl group to be strengthened slightly, this reversal of reactivity may be further evidence of an activating polar effect [17] or of the nucleophilic character of the methyl radical. However, it is hard to explain the relatively low reactivity of the β-position to methyl radicals (the normal polar effect could explain the low reactivity to the other radicals), in these terms and variations in the efficiency of the iodine abstraction step may be affecting the results.

TABLE 8

Approximate relative selectivities of methyl, trifluoromethyl, and trichloromethyl radicals

			$RS\delta^x$	90 °C	
	H	CH_2	CH_2	CH_2	CH_3
$CF_3\cdot$		1	14	14	1
$CH_3\cdot$		1	10	10	1
$CCl_3\cdot$		1	90	90	1
	F	CH_2	CH_2	CH_2	CH_3
$CF_3\cdot$		2	2	14	1
$CH_3\cdot$		8	10	10	1
$CCl_3\cdot$		7		90	1
	CF_3	CH_2	CH_2	CH_2	CH_3
$CF_3\cdot$		0.1	2	14	1
$CH_3\cdot$		1.3	3	10	1
$CCl_3\cdot$		0.6	11	90	1

The values are rounded off and adjusted to ensure consistancy between different sets of readings.

The results show that it is possible to obtain Arrhenius parameters for hydrogen abstraction by trifluoromethyl radicals from each individual site in a 1-substituted butane. The results obtained fit in very well with earlier work with trichloromethyl radicals, and with studies involving trifluoromethyl radicals reacting with substituted methanes and ethanes. Attempts to obtain similar data for methyl radicals have not been successful although qualitative ' relative-selectivity ' data has been obtained.

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