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Free-radical Addition to Olefins

Part 26.—Kinetics of the Addition of Trifluoromethyl Radicals to Acetylene and Substituted Acetylenes[1]

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Absolute Arrhenius parameters have been determined for the addition of trifluoromethyl radicals to acetylene, propyne, but-2-yne, 1,1,1-trifluoropropyne and hexafluorobut-2-yne by a competitive method using the previously determined Arrhenius parameters for the addition of trifluoromethyl radicals to ethylene as standard.

X[a]	$k_X/k_{C_2H_2}$ (164 °C)	E_{act}/kcal mol^{-1}	log$A$/dm^3 mol^{-1} s^{-1}
$H\overset{\downarrow}{C}\equiv CH$	1	5.00 ± 0.30	8.70 ± 0.25
$H\overset{\downarrow}{C}\equiv CCH_3$	5.2[b]	3.45 ± 0.28[b]	8.63 ± 0.08[b]
$H\overset{\downarrow}{C}\equiv CCF_3$	0.49	5.10 ± 0.26	8.44 ± 0.13
$CH_3\overset{\downarrow}{C}\equiv CCH_3$	2.0	4.36 ± 0.30	8.68 ± 0.16
$CF_3\overset{\downarrow}{C}\equiv CH$	0.043	6.61 ± 0.33	8.13 ± 0.18
$CF_3\overset{\downarrow}{C}\equiv CCF_3$	0.068	5.86 ± 0.38	7.95 ± 0.06

1 cal ≡ 4.1845 J.

[a] Arrow shows site of attack; [b] sum of attack at both sites in propyne.

Both the activation energies and the A-factors are larger than those for the addition of trifluoromethyl radicals to similarly substituted olefins. As a result of these opposing effects the rates of addition are similar.

The first studies of the addition of trifluoromethyl radicals to acetylenes were those of Haszeldine.[2, 3] The initial paper reported the thermal and photochemical addition of trifluoromethyl iodide to acetylene itself and the second paper reported the photochemical addition of trifluoromethyl iodide to 1,1,1-trifluoropropyne yielding 1,1,1,4,4,4-hexafluoro-2-iodobut-2-ene together with some telomer. No kinetic data were reported. In their important compilation of kinetic data of gas-phase addition reactions Kerr and Parsonage[4] record only four determinations of the rate of addition of methyl radicals to acetylenes, three to acetylene itself[5-7] and one to propyne.[8] Only one paper dealing with trifluoromethyl radical addition to acetylenes is reported, and this work by Szwarc and co-workers[9] describes the determination of the overall rate of addition of trifluoromethyl radicals to acetylene, propyne and but-2-yne. The work was put on an absolute scale by competition with hydrogen abstraction from 2,3-dimethylbutane.

Since the compilation of kinetic data[4] was complete Kerr has re-examined the kinetics of the addition of methyl radicals to ethylene and acetylene.[10] The early work suggested that at temperatures around 150 °C the rates were similar. The recent work confirms this but shows that both Arrhenius parameters are larger for the addition to acetylene ($\log k_{C_2H_2} = 8.78 \pm 0.2 - 7.7 \pm 1.5/2.303$ $\boldsymbol{RT}$ dm^3 mol s^{-1}) than ethylene ($\log k_{C_2H_4} = 8.22 \pm 0.5 - 7.3 \pm 1.0/2.303$ $\boldsymbol{RT}$ dm^3 mol s^{-1}). Cationic addition to acetylenes in solution is well established as proceeding substantially slower than addition to similarly substituted olefins (Br$^+$ adds to RCH$\equiv$CHR′ anything from 20 to 5×10^4 faster than to RC$\equiv$CR′).[11] Taking these results together it would be expected that electrophilic radicals like trifluoromethyl would add more readily to olefins than to acetylenes. Qualitative evidence that this is so comes from the researches of Kharasch who found that trichloromethyl radicals add faster to an alk-1-ene than to an alk-1-yne.[12] The only quantitative data are those of Szwarc and co-workers referred to above. The Arrhenius parameters quoted by Szwarc are based on only three temperatures and are unlikely to be very accurate,[9] more especially as the competitive method these workers were using has been questioned.[13] However, it has been our finding that although Arrhenius parameters differ substantially from Szwarc's we have invariably found similar relative reactivity.

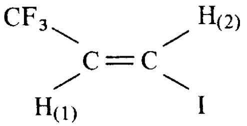
Apart from Szwarc's work there are no kinetic data for the addition of trifluoromethyl radicals to acetylenes and confirmation of the high pre-exponential terms would be of considerable importance. In addition, this work is intended to be an extension of our study of directive effects in free radical addition reactions.[14] There are, as far as we are aware, no kinetic data for the addition of radicals to specific sites in unsymmetrical acetylenes and only two studies of the stereochemistry of the adducts formed by the addition of radicals to acetylenes.

EXPERIMENTAL AND RESULTS

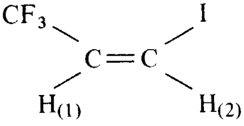
The experimental method has been described in previous papers.[15] The light source was a 100 W medium-pressure mercury arc. Acetylene, obtained from an ordinary commercial cylinder, was bubbled through sulphuric acid to remove traces of acetone, and then passed through a tower of sodium hydroxide. The gas used in the experiments showed only a single peak in the gas chromatogram. The substituted acetylenes were commercial products which, apart from trap-to-trap distillation, were used without further purification. The trifluoromethyl iodide was supplied by Bristol Organics and was stored in the dark.

ACETYLENE

In a preliminary preparative experiment trifluoromethyl iodide and acetylene were photolysed at 150 °C for 2 h. The g.l.c. showed two product peaks which mass spectrometry showed to have the same mass ($C_3H_2F_3I$ $m/e = 222$ M$^+$). A further series of preparative runs were then completed in order to distinguish between the isomers by n.m.r. spectroscopy. Only the major adduct was obtained in sufficient quantity for spectroscopic examination. This showed two doublets of quartets in the ^{1}H n.m.r., $\delta = 6.74$ ppm, $J_{CF_3H_{(1)}} = 6$ Hz; $J_{H_{(2)}H_{(1)}} = 15$ Hz; $\delta = 7.32$ ppm, $J_{CF_3H_{(2)}} = 2$ Hz; $J_{H_{(2)}H_{(1)}} = 15$ Hz which is consistent with structure I,[16] and the minor product must therefore have structure II.



I (*E*)



II (*Z*)

TABLE 1.—ADDITION OF TRIFLUOROMETHYL RADICALS TO ACETYLENE

$[CF_3I] = 3.3 \times 10^{-3}$ mol dm^{-3}, $[C_2H_2] = 4.5 \times 10^{-4}$ mol dm^{-3}.

T/K	t/h	$\frac{[Z\text{-}C_3H_2F_3I]}{[E\text{-}C_3H_2F_3I]}$
323	4.1	0.076
345	3.35	0.087
367	3.0	0.10
393	2.0	0.11
411	1.35	0.12
437	1.2	0.13

A least-squares plot of log II/I against 10^3 K/T gave a straight line of gradient -0.29 ± 0.02 and intercept -0.20 ± 0.05.

A series of runs in which the acetylene concentration was varied from 4.3×10^{-4} to 17.3×10^{-4} mol dm^{-3} showed the ratio of the Z and E isomers to be constant.

A second series of experiments was completed in which ethylene was an additional reactant.

TABLE 2.—COMPETITIVE ADDITION OF TRIFLUOROMETHYL RADICALS TO ETHYLENE AND ACETYLENE

$[CF_3I] = 4.4 \times 10^{-3}$ mol dm^{-3}, $[C_2H_2] = 1.3 \times 10^{-3}$ mol dm^{-3}, $[C_2H_4] = 3.9 \times 10^{-4}$ mol dm^{-3}.

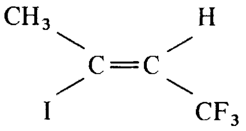
T/K	t/h	$\frac{[E\text{-}C_3F_3H_2I]}{[C_3F_3H_4I]}$	$\frac{[Z\text{-}C_3F_3H_2I]}{[C_3F_3H_4I]}$	$\frac{\Sigma[C_3F_3H_2I]}{[C_3F_3H_4I]}$
351	1.1	0.069	0.0063	0.075
371	0.3	0.075	0.0078	0.084
393	0.2	0.093	0.0102	0.102
417	0.15	0.108	0.0132	0.120
423	0.11	0.114	0.0144	0.126
453	0.07	0.126	0.0171	0.141

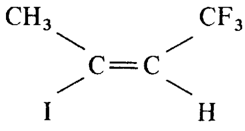
A least-squares plot of log ($[E\text{-}C_3H_2F_3I]/[C_3H_4F_3I]$) against 10^3 K/T gave a gradient of -0.43 ± 0.025 and an intercept of 0.58 ± 0.06. A similar plot of log$[Z\text{-}C_3H_2F_3I]/[C_3H_4F_3I]$ against 10^3 K/T gave a gradient of -0.73 ± 0.025 and an intercept of 0.38 ± 0.06. A third plot of log$\Sigma[C_3H_2F_3I]/[C_3H_4I]$ against 10^3 K/T gave a gradient of -0.46 ± 0.025 and an intercept of 0.7 ± 0.06.

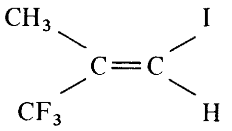
A further series of experiments was carried out in which the acetylene concentration was varied while all the other variables (light, temperature and CF_3I) were kept constant. Within experimental error the product ratio $[E\text{-}C_3H_2F_3I]/[Z\text{-}C_3H_2F_3I]$ remained constant.

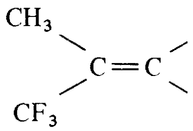
PROPYNE

There are four expected adducts from the additions of trifluoromethyl iodide to propyne:


III


IV


V


VI

Preparative g.l.c. separated two product peaks both of which had parent ions in the mass spectrum ($m/e = 236$) corresponding to the adducts. The ^{1}H n.m.r. spectrum of the major peak consisted of a doublet of quartets at $\delta = 2.67$ ppm ($J_{\mathrm{CF_3CH_3}} = 2.1$ Hz; $J_{\mathrm{H,CH_3}} = 1.55$ Hz) and a quartet of quartets at $\delta = 6.36$ ppm ($J_{\mathrm{CH_3,H}} = 1.5$ Hz; $J_{\mathrm{CF_3,H}} = 7.7$ Hz). In addition there were two low-intensity peaks at $\delta = 1.97$ ppm and $\delta = 7.28$ ppm. The ratio of the high and low intensity lines was 15:1. The ^{19}F n.m.r. spectrum consisted of a doublet of quartets at $\phi = 59.17$ ppm ($J_{\mathrm{CH_3,CF_3}} = 2.1$ Hz; $J_{\mathrm{CF_3,H}} = 7.7$ Hz) together with a low-intensity doublet of quartets $\phi = 69.17$ ppm ($J_{\mathrm{CH_3CF_3}} = 0.3$ Hz; $J_{\mathrm{H,CF_3}} = 1.7$ Hz). The spectra correspond to a mixture of III (main product) and V. The ^{1}H n.m.r. spectrum of the smaller peak in the gas chromatogram consisted of a doublet of quartets at $\delta = 2.69$ ppm ($J_{\mathrm{CH_3,CF_3}} = 2.2$ Hz; $J_{\mathrm{CH_3,H}} = 1.6$ Hz) together with a quartet of quartets at $\delta = 6.24$ ppm ($J_{\mathrm{CF_3,H}} = 7.2$ Hz; $J_{\mathrm{CH_3H}} = 1.5$). The ^{19}F n.m.r. consisted of a doublet of quartets at $\phi = 61.16$ ppm ($J_{\mathrm{CH_3,CF_3}} = 2.2$ Hz; $J_{\mathrm{CF_3,H}} = 7.2$ Hz). These spectra correspond to IV. Isomer VI if formed was present in too small a proportion to be identified.

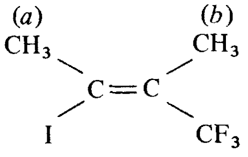
TABLE 3.—COMPETITIVE ADDITION OF TRIFLUOROMETHYL RADICALS TO ETHYLENE AND PROPYNE
$[\mathrm{CF_3I}] = 3.26 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{CH_3C{\equiv}CH}] = 8.6 \times 10^{-3}$ mol dm^{-3},
$[\mathrm{CH_2{=}CH_2}] = 3.9 \times 10^{-4}$ mol dm^{-3}.

T/K	t/h	$\frac{[Z\text{-}\mathrm{C_4H_4F_3I}]}{[\mathrm{C_3H_4F_3I}]}$	$\frac{[E\text{-}\mathrm{C_4H_4F_3I}]}{[\mathrm{C_3H_4F_3I}]}$	$\frac{\Sigma[\mathrm{C_4H_4F_3I}]}{[\mathrm{C_3H_4F_3I}]}$
435	0.07	0.46	0.047	0.51
427	0.13	0.45	0.043	0.49
405	0.16	0.43	0.033	0.46
385	0.3	0.44	0.037	0.47
365	0.45	0.42	0.028	0.44
383	1.3	0.39	0.022	0.41
314	2.3	0.38	0.023	0.40

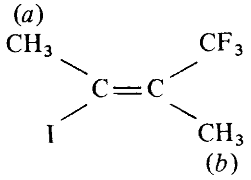
A least-squares plot of $\log([Z\text{-}\mathrm{C_4H_4F_3I}]/[\mathrm{C_3H_4F_3I}])$ against 10^3 K/T gave a gradient of -0.095 ± 0.009 and an intercept of 0.22 ± 0.02; a similar plot of $\log([E\text{-}\mathrm{C_4H_4F_3I}]/[\mathrm{C_3H_4F_3I}])$ gave a slope of -0.37 ± 0.06 and an intercept of -0.17 ± 0.15; a third plot of $\log(\Sigma[\mathrm{C_4H_4F_3I}]/[\mathrm{C_3H_2F_3I}])$ gave a slope of -0.12 ± 0.01 and an intercept of 0.33 ± 0.03 and a fourth plot of $\log([E\text{-}\mathrm{C_4H_4F_3I}]/[Z\text{-}\mathrm{C_4H_4F_3I}])$ gave a slope of -0.25 ± 0.06 and an intercept of -0.43 ± 0.15.

BUT-2-YNE

In preliminary experiments in which trifluoromethyl iodide was photolysed in the presence of ethylene and but-2-yne, three adduct products were detected, two isomers with $m/e = 250$ $M^+(C_5H_6F_3I)$ and the ethylene adduct. The isomers of $m/e = 250$ were separated by preparative g.l.c. The ^1H n.m.r. spectrum of the major product had a broad quartet at $\delta = 2.12$ ppm ($J_{CH_3(a), CH_3(b)} = 1.6$ Hz), together with a complex set of lines at $\delta = 2.82$ ppm which could be assigned to the splitting of the $CH_3(a)$ protons by those of $CH_3(b)$ and the fluorines of the CF_3 [the coupling constant between the fluorine atoms and the protons of $CH_3(b)$ is small]. The ^{19}F n.m.r. spectrum consisted



VII



VIII

of a quartet at $\phi = 58.16$ ppm ($J_{CH_3(a), CF_3} = 2.3$ Hz). The ^1H n.m.r. spectrum of the minor isomer consisted of a broad quartet, $\delta = 1.91$ ppm ($J_{CH_3(a), CH_3(b)} = 1.2$ Hz), together with a complex set of lines at $\delta = 2.7$ ppm. The ^{19}F n.m.r. spectrum consisted of a quartet at $\phi = 62.95$ ppm ($J_{CH_3(a), CF_3} = 2.5$ Hz). These n.m.r. spectra, when compared with those of the isomers for the addition to propyne, lead to assigning the major isomer, structure VII and the minor product structure VIII.

TABLE 4.—COMPETITIVE ADDITION OF TRIFLUOROMETHYL RADICALS TO ETHYLENE AND TO BUT-2-YNE

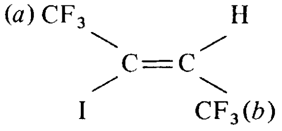
$[CF_3I] = 4.35 \times 10^{-3}$ mol dm^{-3}, $[CH_3C{\equiv}CCH_3] = 8.64 \times 10^{-4}$ mol dm^{-3}, $[CH_2{=}CH_2] = 3.9 \times 10^{-4}$ mol dm^{-3}.

T/K	t/h	$\frac{[Z\text{-}C_5H_6F_3I]}{[C_3H_4F_3I]}$	$\frac{[E\text{-}C_5H_6F_3I]}{[C_3H_4F_3I]}$	$\frac{\Sigma[C_5H_6F_3I]}{[C_3H_4F_3I]}$
327	2.4	0.18	0.031	0.21
336	2.1	0.21	0.041	0.25
360	1.4	0.23	0.043	0.28
383	1.15	0.25	0.054	0.30
408	1.0	0.29	0.054	0.34
436	0.4	0.34	0.072	0.41
479	0.1	0.37	0.086	0.45

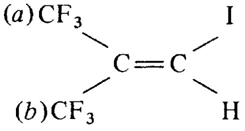
A least-squares plot of $\log([Z\text{-}C_5H_6F_3I]/[C_3H_4F_3I])$ against 10^3 K/T gave a gradient of -0.31 ± 0.02 and an intercept of 0.57 ± 0.05; a similar plot of $\log([E\text{-}C_5H_6F_3I]/[C_3H_4F_3I])$ had a slope of -0.39 ± 0.05 and an intercept of 0.07 ± 0.14; a third plot of $\log(\Sigma[C_5H_6F_3I]/[C_3H_4F_3I])$ had a gradient of -0.32 ± 0.02 and an intercept of 0.68 ± 0.06. The fourth plot ($\log[E\text{-}C_5H_6F_3I]/\log[Z\text{-}C_5H_6F_3I]$) had a gradient of -0.09 ± 0.04 and an intercept of -0.47 ± 0.11.

1,1,1-TRIFLUOROPROPYNE

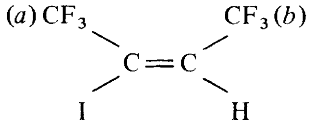
In preliminary experiments trifluoromethyl iodide was photolysed in the presence of 1,1,1-trifluoropropyne and four adduct products were identified. Three were isomers, m/e 290 (M^+ C_4HF_6I) and the fourth with a higher mass m/e 384 (M^+ $C_7H_2F_9I$). The ^1H n.m.r. spectrum of the first isomer to be eluted, the major isomer, consisted of a quartet of quartets at $\delta = 7.18$ ppm ($J_{CF_3(a),H} = 1.4$ Hz; $J_{CF_3(b),H} = 6.5$ Hz). The ^{19}F n.m.r. spectrum consisted of two sets of double quartets at $\phi = 62.34$ ppm ($J_{H,CF_3(b)} = 6.5$ Hz; $J_{CF_3(a),CF_3(b)} = 1.4$ Hz; $J_{CF_3(b),CF_3(a)} = 1.4$ Hz; $J_{CF_3(a),H} = 1.4$ Hz). These spectra are consistent with structure IX.



IX

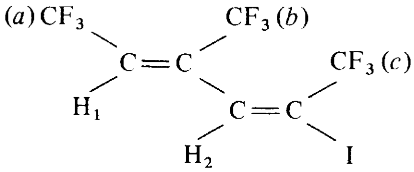


X



XI

The ^1H n.m.r. spectrum of the second product eluted consisted of a quartet at $\delta = 8.24$ ppm ($J_{CF_3(a),H} = 1.5$ Hz) and the ^{19}F n.m.r. spectrum consisted of a quartet of doublets at $\phi = 64.7$ ppm ($J_{H,CF_3(a)} = 1.5$ Hz; $J_{CF_3(a),CF_3(b)} = 6.5$ Hz) and a quartet at $\phi = 61.9$ ppm ($J_{CF_3,CF_3(b)} = 6.7$ Hz). These spectra are consistent with structure X. The ^1H n.m.r. spectrum of the third product eluted consisted of a quartet at $\delta = 6.89$ ppm ($J_{CF_3(a),H} = 8.1$ Hz). The ^{19}F n.m.r. spectrum consisted of a doublet of quartets at $\phi = 59.1$ ppm ($J_{CF_3(a),CF_3(b)} = 11.2$ Hz; $J_{H,CF_3(a)} = 8.1$ Hz) and a quartet at $\phi = 60.9$ ppm ($J_{CF_3(a),CF_3(b)} = 11.2$ Hz). These spectra are consistent with structure XI. The ^1H n.m.r. spectrum of the remaining product with the higher molecular weight consisted of a quartet at $\delta = 6.46$ ppm ($J_{CF_3(a),H_1} = 7.8$ Hz) and a broad peak at $\delta = 7.2$ ppm. The ^{19}F n.m.r. spectrum had a doublet at $\phi = 62.1$ ppm and two singlets at $\phi = 66.97$ and 67.28 ppm. These two spectra correspond to structure XII.



XII

In a series of runs at different temperatures trifluoroiodomethane and 1,1,1-trifluoropropyne were photolysed in the temperature range 56-186 °C. The products consisted of the E- and Z-isomers of $CF_3CH{=}CICF_3$ and $(CF_3)_2C{=}CHI$; the telomer $C_7H_2F_9I$ was only present in the high conversion runs used for structural analysis.

A least-squares plot of $\log([E\text{-}CF_3CH{=}CICF_3]/[Z\text{-}CF_3CH{=}CICF_3])$ against 10^3 K/T gave a line of gradient -0.16 ± 0.01 and an intercept of -0.43 ± 0.03; a similar plot of $\log\{[(CF_3)_2C{=}CHI]/\Sigma[CF_3CH{=}CICF_3]\}$ against 10^3 K/T gave a gradient of -0.34 ± 0.05 and an intercept of -0.3 ± 0.1. A second set of low conversion competitive runs was completed using trifluoroiodomethane (43.5×10^{-4} mol dm^{-3}), 1,1,1,-trifluoropropyne (13.0×10^{-4} mol dm^{-3}) and ethylene (3.9×10^{-4}

TABLE 5.—ADDITION OF TRIFLUOROIODOMETHANE TO 1,1,1-TRIFLUOROPROPYNE
$[CF_3I] = 32.6 \times 10^{-4}$ mol dm^{-3}, $[CF_3C{\equiv}CH] = 8.6 \times 10^{-4}$ mol dm^{-3}.

T/K	t/h	$\frac{[(CF_3)_2C{=}CHI]}{[Z\text{-}CF_3CH{=}CICF_3]}$	$\frac{[E\text{-}CF_3CH{=}CICF_3]}{[Z\text{-}CF_3CH{=}CICF_3]}$
329	4	0.053	0.12
360	2	0.061	0.14
391	1.10	0.077	0.14
418	0.27	0.097	0.16
459	0.15	0.10	0.16

mol dm^{-3}). The consumption of ethylene was kept below 5% and the temperature varied over a 150 degree range. Three products were obtained in sufficient quantities for accurate analysis, $CF_3CH_2CH_2I$; Z-$CF_3CH{=}CICF_3$ and $C_6H_5F_6I$. The latter compound was identified by its mass spectrum as the cross telomer $CF_3CH{=}C(CF_3)CH_2CH_2I$ but it was not possible to determine its stereochemistry.

TABLE 6.—COMPETITIVE ADDITION OF TRIFLUOROIODOMETHANE TO ETHYLENE AND 1,1,1-TRIFLUOROPROPYNE

T/K	t/h	$\frac{[Z\text{-}CF_3CH{=}CICF_3]}{[CF_3CH_2CH_2I]}$	$\frac{[C_6H_5F_6I]}{[CF_3CH_2CH_2I]}$
318	3.4	0.044	0.010
338	2.2	0.053	0.012
348	1.45	0.057	0.015
360	1.15	0.060	0.021
393	0.40	0.079	0.016
425	0.16	0.086	0.014
447	0.08	0.10	0.022
473	0.02	0.12	0.020

A least-squares plot of $\log(\{[Z\text{-}CF_3CH{=}CICF_3]+[C_6H_5F_6I]\}/\{[CF_2CH_2CH_2I]/[CH_2{=}CH_2]/[CF_3C{\equiv}CH]\})$ against 10^3 K/T gave a gradient of -0.36 ± 0.02 and an intercept of -0.11 ± 0.06. By combining the results from tables 5 and 6 the absolute Arrhenius parameters for the addition of trifluoromethyl radicals to both ends of 1,1,1-trifluoropropyne could be calculated using the parameters we have previously determined for ethylene.[15] (These are given in table 10.)

HEXAFLUOROBUT-2-YNE

When it was attempted to study the addition of trifluoromethyl radicals to hexafluorobut-2-yne competitively with ethylene, the consumption of ethylene was relatively so rapid that it was impossible to use unintegrated rate expressions. Instead therefore hexafluorobut-2-yne was studied competitively with trifluoroethylene. Trifluoroiodomethane (3.81×10^{-3} mol dm^{-3}), hexafluorobut-2-yne (5.85×10^{-4} mol dm^{-3}) and trifluoroethylene (5.85×10^{-4} mol dm^{-3}) were photolysed together for 2.3 h. Three products were isolated, the two simple adducts CF_3CHFCF_2I and $(CF_3)_2C{=}CICF_3$ together with the one to one telomer $(CF_3)_2C{=}C(CF_3)CHFCF_2I$. A series of runs of varying time and temperature was then completed.

TABLE 7.—COMPETITIVE ADDITION OF TRIFLUOROIODOMETHANE TO TRIFLUOROETHYLENE AND HEXAFLUOROBUT-2-YNE

T/K	T/h	$\frac{[(CF_3)_2C{=}ClCF_3]}{[CF_3CHFCF_2I]}$	$\frac{[C_7HF_{12}I]}{[CF_3CHFCF_2I]}$
327	4.30	0.63	—
343	3.35	0.64	0.062
367	2.50	0.76	0.046
383	2.30	0.77	0.038
393	2.10	0.79	0.055
433	1.10	0.84	0.050
473	0.14	0.99	0.050

A least-squares plot of $\log(\{[(CF_3)_2C{=}ClCF_3]+[C_7HF_{12}I]\}/\{[CF_3CHFCF_2I][CHF{=}CF_2]/[CF_3C{\equiv}CCF_3]\})$ against 10^3 K/T gave a line with a gradient -0.23 ± 0.02 and an intercept of 0.50 ± 0.06. Using our previous data for the relative rate of addition of trifluoromethyl radicals to trifluoroethylene and our absolute Arrhenius parameters for ethylene, absolute parameters could be calculated.

DISCUSSION

The mechanism of the photochemical addition of trifluoromethyl iodide to alkynes is exactly similar to the analogous addition to alkenes

$$CF_3I \rightarrow CF_3\cdot + I\cdot \tag{1}$$

$$CF_3 + A \rightarrow CF_3A\cdot \tag{2}$$

$$CF_3A\cdot + CF_3I \rightarrow CF_3AI + CF_3\cdot. \tag{3a}$$

The initiation step is followed by the chain-carrying steps (2) and (3), in which A stands for alkyne. In many of the present experiments the alkyne was reacted competitively with an alkene (E).

$$CF_3\cdot + E \rightarrow CF_3E\cdot \tag{2e}$$

$$CF_3E\cdot + CF_3I \rightarrow CF_3EI + CF_3\cdot. \tag{3e}$$

The chains are long, and making the normal steady state assumptions we have for small conversions:

$$\frac{[CF_3AI]_f}{[CF_3EI]_f} = \frac{k_{2a}[A]_i}{k_{2e}[E]_i}$$

where the subscripts f and i stand for final and initial, respectively. In the present work E was either ethylene itself or trifluoroethylene for both of which the value of Arrhenius parameters A_{2e} and E_{2e} are known^2 so that the corresponding Arrhenius parameters A_{2e} and E_{2e} could be determined and listed in table 8.

The addition of trifluoromethyl iodide to an alkyne can yield two geometric isomers (E and Z) and, if the alkyne is unsymmetric, this will lead to four isomers in all. However, with propyne only three isomers were identified. 1,1,1-Trifluoropropyne yielded the expected three isomers (there is only one isomer when the $CF_3\cdot$ radical addition occurs at the CF_3-end). When reacted by itself, 1,1,1-trifluoropropyne yielded

TABLE 8.—ABSOLUTE ARRHENIUS PARAMETERS AND RELATIVE RATES FOR THE ADDITION OF $CF_3\cdot$ RADICALS TO ALKYNES AND ALKENES

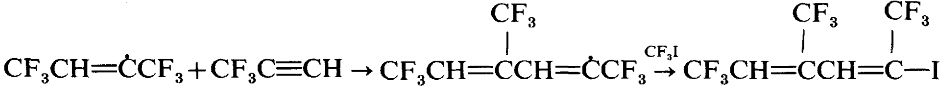
acetylenes			
a	$\log A_2^a$	E_2^a	$k_2^a/k_2^{C_2H_2}$ (164 °C)
$H—C{\equiv}C—H$	8.70	5.00	1
$H—C{\equiv}C—CH_3$	8.63	3.45	5.2
$H—C{\equiv}C—CF_3$	8.44	5.10	0.49
$CH_3—C{\equiv}C—CH_3$	8.68	4.36	2.0
$CF_3—C{\equiv}C—H$	8.13	6.61	0.043
$CF_3—C{\equiv}C—CF_3$	7.95	5.86	0.068

	olefins			ratios C≡C/C≡C		
e	$\log A_2^e$	E_2^e	$k_2^e/k_2^{C_2H_4}$	$\log A_2^e/A_2^a$	E_2^a-E_2^e	k_2^e/k_2^a (164 °C)
$H—CH{=}CH—H$	8.00	2.85	1	−0.70	2.15	2.4
$H—CH{=}CH—CH_3$	7.92	1.98	2.3	−0.71	1.47	1.0
$H—CH{=}CH—CF_3$	7.76	3.10	0.43	−0.68	2.00	1.95
$CH_3—CH{=}C(CH_3)_2$	7.48	0.90	2.9	−1.20	3.46	3.26
$CF_3—CH{=}CH—H$	7.74	5.76	0.18	−0.42	0.85	9.0
$CF_3—CH{=}CH—CF_3$	—	—	—	—	—	—

a 1:1 telomer $CF_3CH{=}C(CF_3)CH{=}CICF_3$ (this was originally observed by Haszeldine)[2] and when reacted competitively with ethylene it yielded the cross-telomer $CF_3CH{=}C(CF_3)CH_2CH_2I$. These telomeric products can probably be attributed to the great reactivity displayed by a vinylic radical in which the α-position carries a trifluoromethyl group ($=C—CF_3$). Exactly similar telomeric products were observed when hexafluorobut-2-yne was reacted competitively with trifluoroethylene. Again the high reactivity of the α-trifluoromethyl vinyl radical is observed. We can represent the telomer formation with 1,1,1-trifluoropropyne as follows:-

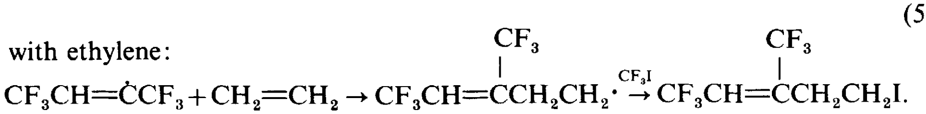
$$CF_3\cdot + CF_3C{\equiv}CH \rightarrow CF_3CH{=}\dot{C}CF_3 \qquad (4)$$

either with itself:



$$CF_3CH{=}\dot{C}CF_3 + CF_3C{\equiv}CH \rightarrow CF_3CH{=}\overset{\overset{CF_3}{|}}{C}CH{=}\dot{C}CF_3 \xrightarrow{CF_3I} CF_3CH{=}\overset{\overset{CF_3}{|}}{C}CH{=}\overset{\overset{CF_3}{|}}{C}—I \qquad (5)$$

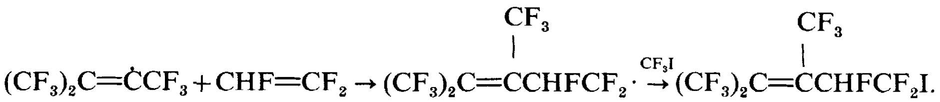
or with ethylene:



$$CF_3CH{=}\dot{C}CF_3 + CH_2{=}CH_2 \rightarrow CF_3CH{=}\overset{\overset{CF_3}{|}}{C}CH_2CH_2\cdot \xrightarrow{CF_3I} CF_3CH{=}\overset{\overset{CF_3}{|}}{C}CH_2CH_2I. \qquad (6)$$

The reaction of hexafluorobut-2-yne with trifluoroethylene is similar:

$$CF_3\cdot + CF_3C{\equiv}CCF_3 \rightarrow (CF_3)_2C{=}\dot{C}CF_3 \qquad (7)$$



$$(CF_3)_2C{=}\dot{C}CF_3 + CHF{=}CF_2 \rightarrow (CF_3)_2C{=}\overset{\overset{CF_3}{|}}{C}CHFCF_2\cdot \xrightarrow{CF_3I} (CF_3)_2C{=}\overset{\overset{CF_3}{|}}{C}CHFCF_2I. \qquad (8)$$

Diadducts in which a second CF_3I molecule adds across the double bond in the primary adduct were not observed in any of these experiments.

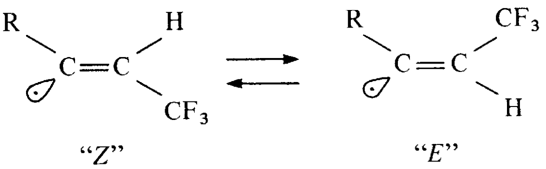
The Arrhenius parameters for the addition of trifluoromethyl radicals to alkynes are compared with the parameters for similarly substituted alkenes in table 8. This table also presents the ratio of rate constants for the two types of addition. A very striking feature is the close similarity of the rate of constants of addition at 164 °C. Attack occurs faster at the alkene than at the alkyne, but the difference in rate is never greater than a factor 9, although within the alkyne series the rates vary by more than an order of magnitude. This shows that substituents have very similar effects on the reactivity of both double and triple bonds and establish that free-radical addition to alkynes and alkenes must be a very similar process. The electrophilic trifluoromethyl radicals add faster to the 1-positions in both propyne and propene and slower to the equivalent position in both 1,1,1-trifluoropropyne and 1,1,1-trifluoropropene than to the corresponding sites in acetylene and ethylene, respectively. The 2-positions in all four unsaturated molecules are less rapidly attacked, the 2-positions in trifluoropropyne and trifluoropropene being particularly unreactive.

In spite of the very similar relative rates of addition at 164 °C, the Arrhenius parameters for addition to the alkynes are substantially different from the parameters for addition to similar sites in the alkenes. The pre-exponential terms are without exception larger for addition to the alkynes than for addition to the alkenes, by a factor of between 2.5 and 5. This increased *A*-factor is offset by an appreciably larger activation energy for the additions to the alkynes. These results are very satisfactory confirmation of theoretical expectation. The large *A*-factors for the alkyne additions are in accordance with simple transition-state theory. Ethylene has a rotation about the carbon–carbon axis which is lacking in acetylene and the entropy of acetylene is therefore considerably less than that of ethylene. In the transition state this distinction disappears and hence the overall entropy of activation $\Delta S^{\ddagger}$ is less in the addition of a radical to an acetylene. Alternatively we can use Benson's group additivity terms to determine the total entropy changes. The calculated ΔS° values for the addition of $CH_3\cdot$ and $CF_3\cdot$ to acetylene to form the propenyl and the 3,3,3-trifluoropropenyl radicals are found to be -25.8 and -34.6 cal mol^{-1} K^{-1}, respectively, referred to the standard state of 1 mol dm^{-3}. Similarly the ΔS° values for the addition of the same radicals to ethylene to form propyl and 3,3,3-trifluoropropyl radicals are found to be -30.0 and -35.3 cal mol^{-1} K^{-1}. These total entropy changes should parallel the entropies of activation and confirm that higher *A*-factors for radical addition to acetylenes are to be expected.

The activation energies for the addition of trifluoromethyl radicals are without exception substantially larger for addition to the alkynes than the corresponding alkenes. This is consistent with the electrophilic character of the trifluoromethyl radical and the known reluctance of electrophiles to add to acetylenes.

The only previous study involving trifluoromethyl radicals where both geometric isomers have been reported in a single qualitative experiment involves the addition of trifluoromethyl iodide to propyne.[16] There are studies of the addition of sulphur radicals to acetylenes ($SF_5\cdot$ and $CH_3S\cdot$), in which both geometric isomers have been isolated. The addition of thiyl radicals to both olefins and acetylenes is known to be reversible, but Heiba and Dessau made the important observation that the addition of $CH_3S\cdot$ radicals to acetylenes was much less reversible than the corresponding addition to olefins.[17] They also observed that the resultant vinyl radical was much more reactive than the corresponding alkyl radical. Szwarc has provided good evidence that the addition of trifluoromethyl radicals to alkenes is not reversible, so the addition to alkynes is even less likely to be reversible.[18]

The interconversion of *E* and *Z* vinyl radicals is known to be very rapid even at −180 °C in solution[19] and, although the size of substituents affects the rate of isomerisation, it is probable that at the temperatures of the present work it was very rapid indeed. If we assume that the rate of iodine abstraction from iodotrifluoromethane is fast and similar for the two vinyl radicals, the proportions of the two adduct geometric isomers will be governed by the equilibrium between the two vinyl radical geometric isomers



In the Experimental section we report the variation of the ratio of the geometric isomer adducts with temperature and hence we can calculate the enthalpy and entropy difference between the vinyl radical geometric isomers. Addition to acetylene is predominantly *trans*, while addition to propyne, but-2-yne and 1,1,1-trifluoropropyne is predominantly *cis*. Table 9 shows that this difference can be attributed to the relative stabilities of the vinyl radicals. These results can be rationalised in terms of intramolecular repulsion. If it is assumed that the single electron (like a lone pair) occupies more space than a hydrogen atom but less space than methyl or a trifluoromethyl group (*i.e.* the effective size of groups is H < lone electron ≪ CH_3 < CF_3) then we would expect the *E*-isomer to predominate for acetylene itself but that the *Z*-isomer would predominate for all the other additions. Similarly the difference in enthalpy between the two radicals derived from but-2-yne is the smallest difference of the series, as required by the intramolecular hypothesis.

TABLE 9.—RATIO OF THE GEOMETRIC ISOMER ADDUCTS AND ΔH° AND ΔS° FOR THE CORRESPONDING VINYL RADICALS

alkyne	product ratio $Z{:}E$, 160 °C	*Z* and *E* vinyl radicals ΔH°/kcal mol^{-1}	ΔS°/cal mol^{-1} K^{-1}
$CH{\equiv}CH$	0.13	−1.33	−1.0
$CH_3C{\equiv}CH$	9.8	1.15	2.0
$CH_3C{\equiv}CCH_3$	4.8	0.42	2.2
$CF_3C{\equiv}CH$	6.2	0.74	2.0

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