Carbene Chemistry. Part 12.[1] Kinetics of the Isomerisation, Addition, and Insertion Reactions of 1,2,2-Trifluoroethylidene

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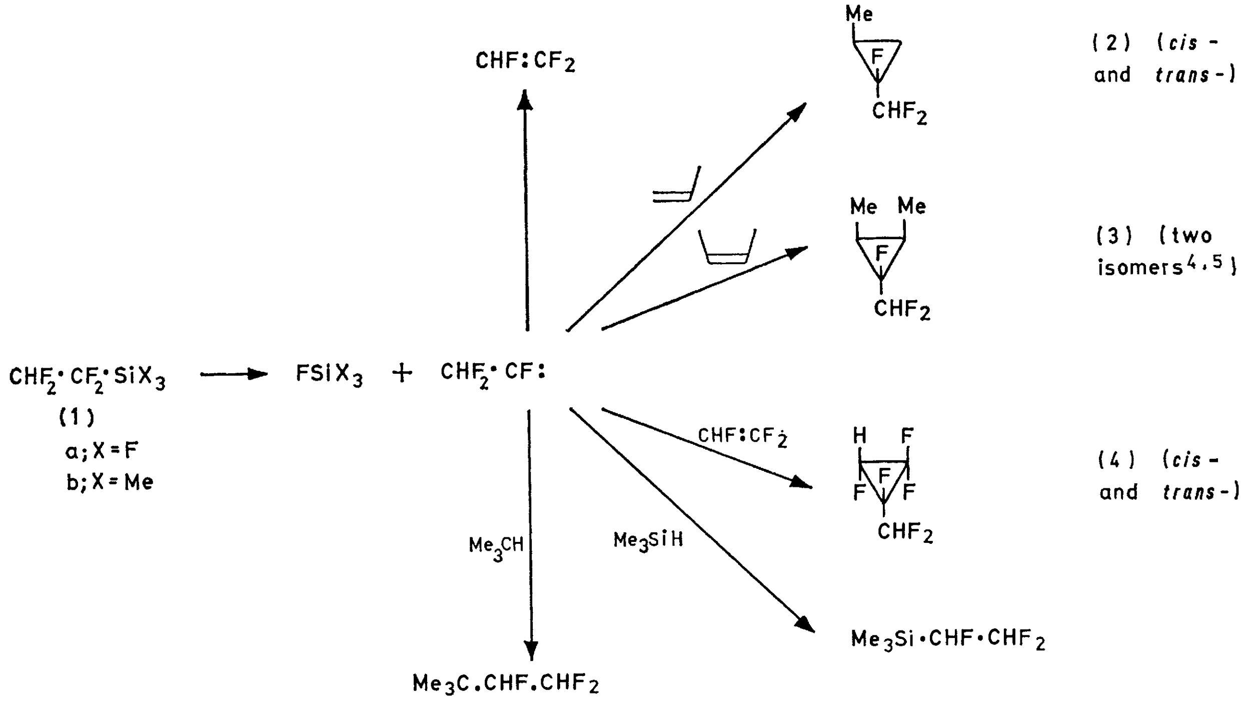
The carbene $CHF_2\cdot CF\colon$ has been generated by pyrolysis of trifluoro- and trimethyl-1,1,2,2-tetrafluoroethylsilane [(1a) and (1b)], and relative rates measured for its addition reactions with propene, *cis*-but-2-ene, and trifluoroethylene, and its insertion reactions with trimethylsilane and isobutane, all relative to the rate of its isomerisation to trifluoroethylene. The isomerisation is a unimolecular reaction in its fall-off region, having $p_{\frac{1}{2}}$ = 125—430 mmHg at 440—623 K. By fitting RRKM (Forst method) predictions to the fall-off plots, using an estimated *A*-factor of $10^{13.4}$ s^{-1}, the activation energy for the isomerisation is found to be *ca.* 96 kJ mol^{-1}. The addition and insertion reactions have *A*-factors which appear to approach the collision rate-constant ($10^{11.4}$ dm^3 mol^{-1} s^{-1}) and activation energies around 47—50 kJ mol^{-1}.

1,2,2-TRIFLUOROETHYLIDENE (difluoromethylfluorocarbene), obtained by α-fluorine elimination from a silicon compound of type $CHF_2\cdot CF_2\cdot Si\lessgtr$, isomerises to trifluoroethylene, and undergoes addition or insertion reactions in the presence of various olefinic or saturated additives.[2] Scheme 1 shows those of the many such reactions studied[1-5] relevant to the present work. Earlier kinetic studies[3,4] showed that the thermal decomposition of the α-fluorosilicon compounds (1a) and (1b) at 413—473 and 573—643 K respectively were unimolecular[3,4] and were consistent with the carbene being in a singlet state.[1,4,5] These studies are now extended to provide kinetic information on the isomerisation, addition, and insertion reactions of the carbene.



SCHEME 1

RESULTS

The analytical techniques described previously[3,4] were used to determine the product distributions obtained from various reactant–additive systems. For each system studied it was established that the overall stoicheiometry was given by equation (1), which is consistent with the Scheme 1. In equation (1), A is the additive and C_2HF_3A is

$$CHF_2CF_2SiX_3 + (1 - x)A \longrightarrow FSiX_3 + xCHF\colon CF_2 + (1 - x)C_2HF_3A \quad (1)$$

the addition or insertion product; in the reactions involving (1a), addition to trifluoroethylene was usually significant even when this olefin was not initially present, and had to be allowed for in checking the stoicheiometry. Results typical of those leading to the above conclusions are illustrated in Figure 1. No indication was obtained of any product arising from the decomposition of chemically activated molecules formed by the carbene addition or insertion reactions.

It has already been established by gas-chromatographic analysis that the disappearance of reactant proceeds with the same first-order rate constant k_1 in the presence of additives as in their absence.[3,4] Since reaction of the

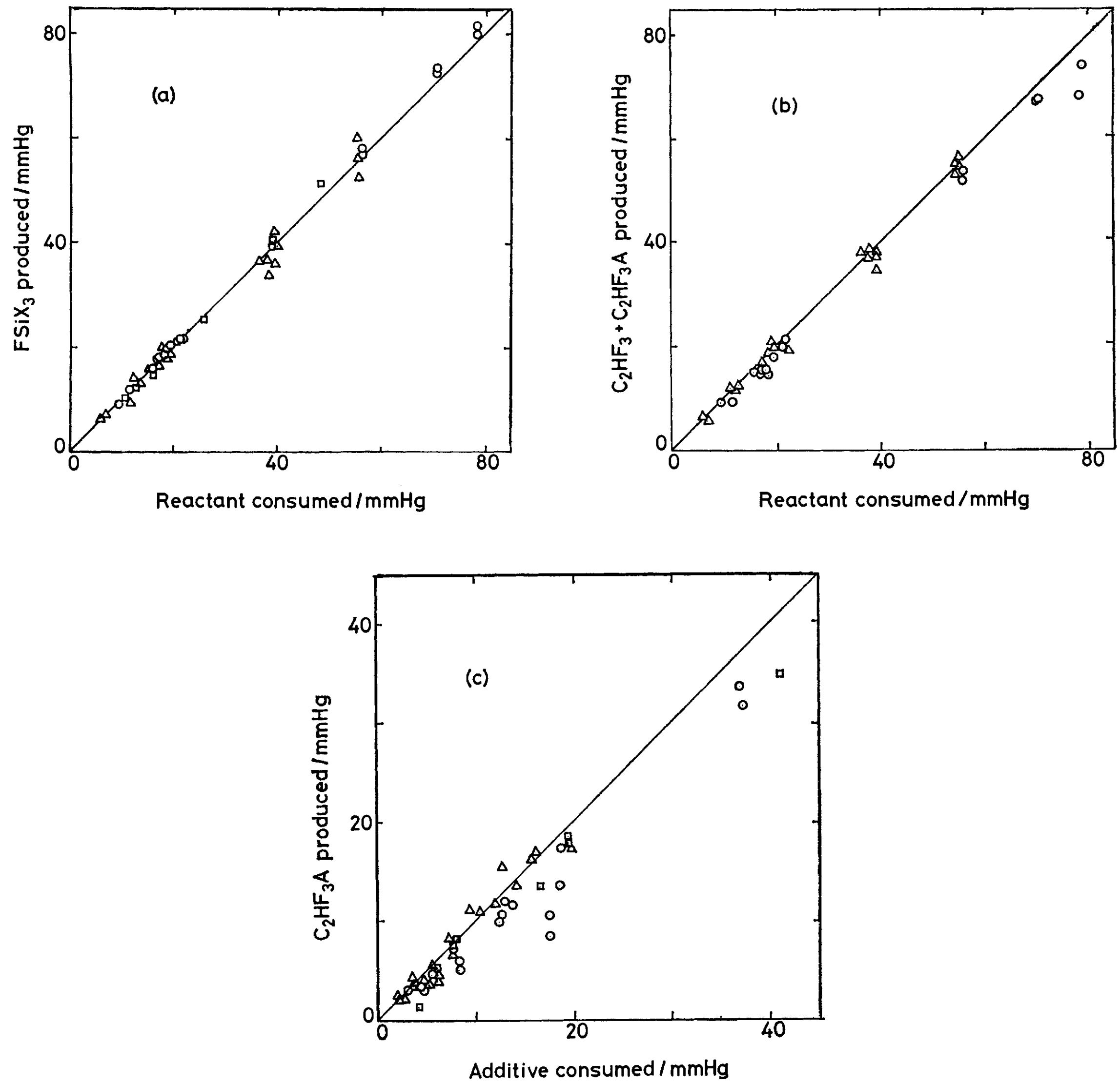


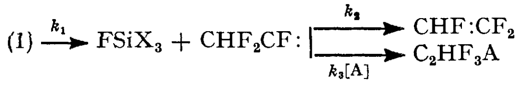
FIGURE 1 Plots demonstrating the stoicheiometry of equation (1); (*a*) $FSiX_3$ produced *vs.* reactant consumed, (*b*) trifluoroethylene plus addition/insertion product produced (plus twice any trifluoroethylene dimer) *vs.* reactant consumed, (*c*) addition/insertion product produced *vs.* additive consumed. In each case the symbol ○ refers to the reactions of (1a) with trimethylsilane, □ to (1a) with propene, and △ to (1b) with *cis*-but-2-ene

carbene with the additive leads to no overall pressure change, whereas isomerisation to trifluoroethylene results in an overall doubling of the pressure, the relative rates of these processes may conveniently be obtained by measurement of the rates of pressure change in the presence and absence of additives. Specifically, the fraction x of carbene which isomerises to trifluoroethylene at any time is given by $x = (dp_t/dt)/(-dp^R_t/dt)$ where p_t is the total pressure and p^R_t the partial pressure of reactant at time t. The numerator in this expression can be determined from the pressure–time curves in the presence of additives, and the denominator can be calculated from the known [3,4] first-order rate constant k_1 for disappearance of the reactant. In order to determine dp/dt, the p–t plots were approximately linearised by various theoretically based transformations, *e.g.* the plots of $\ln(p_0 + \bar{x}p^R_0 - p_t)$ against time, where $\bar{x}$ is a roughly estimated average value (note that $\bar{x}$ varies with time since the total pressure and pressure of additive vary). It was found, in fact, that the most reproducible and self-consistent results were obtained for the initial stages of the reaction, and we therefore discuss only the *initial* product distribution as a function of reactant and additive pressures. This was most conveniently obtained from equation (2), where p^A_0 is the initial pressure of additive; empirically, plots of $\ln(2p^R_0 + p^A_0 - p_t)$ *vs.* t

$$(x)_{t=0} = \frac{[d\ln(2p^R_0 + p^A_0 - p_t)/dt]_{t=0}}{k_1} \qquad (2)$$

were linear for long enough to enable accurate initial slopes to be obtained.

If Scheme 1 were interpreted on the basis of a simple competition between first-order isomerisation and second-order reaction with an additive as shown in Scheme 2, then the product composition would be given by equations (3) and (4). Thus the function $(1 - x)/x[A]$ should be independent of reactant and additive pressures at a given temperature. In fact, the function shows a marked dependence on these pressures (Figure 2) and even varies



SCHEME 2

with the pressure of added inert gases (CF_4, SiF_4). It is, however, approximately constant for a given *total* pressure in the system, irrespective of the composition, and this suggests that some sort of energy transfer process is involved. Specifically, it will be shown below that the results are entirely consistent with the isomerisation of the carbene being a thermal unimolecular process in its fall-off region, the effect of inert gases being to increase the rate-constant towards its limiting high-pressure value. The isomerisation of trifluoroethylidene would indeed be expected to be in its fall-off region at the experimental pressures, by com-

$$\frac{d[C_2HF_3A]/dt}{d[CHF{:}CF_2]/dt} = \frac{1 - x}{x} = \frac{k_3[A]}{k_2} \qquad (3)$$

or

$$(1 - x)/x[A] = k_3/k_2 \qquad (4)$$

parison with other species containing a similar number of atoms. A different sort of inert gas effect would involve the de-energisation of carbenes carrying excess energy from the initial decomposition reaction. However, the increasing relative yield of olefin at higher temperatures implies that the isomerisation reaction has a higher activation energy than the addition/insertion reactions. If chemically activated reactions were occurring, the addition of inert gas

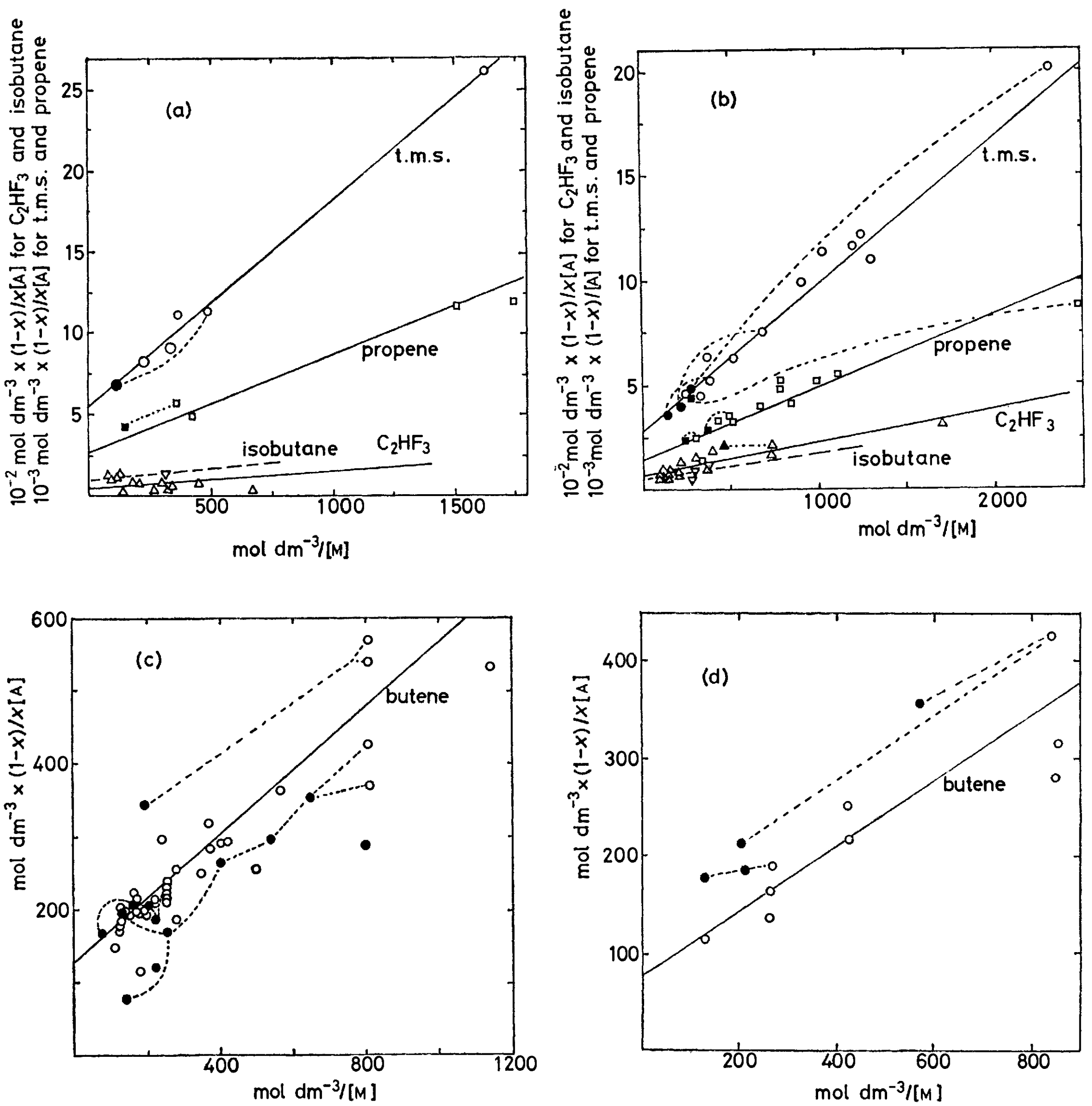


FIGURE 2 Plots of $(1 - x)/x[A]$ *vs.* 1/(total pressure); the straight lines on each plot are drawn with the same S/I (see text and Table 1). Filled points represent runs with added inert gas, and broken lines link runs with approximately constant reactant and additive pressures but varying inert gas pressures. (*a*) (1a) at *ca.* 440 K with trimethylsilane (t.m.s.) (reactant : additive ratio from 2 : 1 to 4 : 1) (○), propene (ratio 1 : 10 to 3 : 1) (□), trifluoroethylene (t.f.e.) (ratio 1 : 5 to 2 : 1) (△), and isobutane (ratio 1 : 5 to 2 : 1) (▽); (*b*) (1a) at 462 K [symbols as for (*a*)]; (*c*) (1b) at 591 K with *cis*-but-2-ene (ratio 1 : 10 to 1 : 1); (*d*) (1b) at 623 K with *cis*-but-2-ene (ratio 1 : 3 to 1 : 1)

would, therefore, be expected to *decrease* the yield of olefin, whereas an increase is, in fact, observed. The carbene can thus be presumed to be formed with internal energy less than the threshold for isomerisation, and to be rapidly thermolysed.

Thus the isomerisation reaction can be written as the more detailed unimolecular reaction scheme shown in equations (5) and (6), in which $\mathrm{CHF_2{\cdot}CF{:}^*}$ represents a

$$\mathrm{CHF_2{\cdot}CF{:}} + \mathrm{M} \underset{k_{2b}}{\overset{k_{2a}}{\rightleftharpoons}} \mathrm{CHF_2{\cdot}CF{:}^*} + \mathrm{M} \tag{5}$$

$$\mathrm{CHF_2{\cdot}CF{:}^*} \xrightarrow{k_{2c}} \mathrm{CHF{:}CF_2} \tag{6}$$

collisionally energised carbene.[6] The rate constants k_{2a} and k_{2c} are energy dependent, but it is useful at this stage to apply the Hinshelwood–Lindemann (HL) treatment, which ignores the variation of k_{2c} and gives (7) for the rate

$$\begin{aligned} \mathrm{d[CHF{:}CF_2]}/\mathrm{d}t &= k_{2c}[\mathrm{CHF_2{\cdot}CF{:}^*}] \\ &= \frac{k_2^{\infty}}{1 + k_2^{\infty}/k_2^{0}[\mathrm{M}]}[\mathrm{CHF_2{\cdot}CF{:}}] \\ \text{where } k_2^{\infty} &= k_{2a}k_{2c}/k_{2b} \text{ and } k_2^{0} = k_{2a} \end{aligned} \tag{7}$$

of formation of trifluoroethylene. Strictly, reversibility of (6) should be considered, but is not likely to have any major effect. Nor are our data sufficiently precise to distinguish between the differing thermal energisation/de-energisation efficiencies of the various species present, and these have all been taken as equal (on a mole-for-mole basis). Using (7) we now obtain (8), which is consistent with the behaviour of the function $(1 - x)/x[\mathrm{A}]$ already observed in Figure 2, *viz.* linear variation with the reciprocal of the total pressure [M] for a given additive at a given temperature, and independence of the reactant : additive : inert gas ratios at a given total pressure.

$$\frac{1 - x}{x[\mathrm{A}]} = \frac{k_3}{k_2^{\infty}} + \frac{k_3}{k_2^{0}} \cdot \frac{1}{[\mathrm{M}]} \tag{8}$$

The ratio *slope/intercept* $= S/I = k_2^{\infty}/k_2^{0}$ should be independent of the nature of the additive, and constant at any given temperature. It is solely a property of the isomerisation reaction of the carbene; in HL theory S/I is in fact $p_{\frac{1}{2}}$ in concentration units, where $p_{\frac{1}{2}}$ is the pressure at which the thermal rate constant k_2 has declined to $\frac{1}{2}k_2^{\infty}$. In more sophisticated theories the plots of $1/k_2$ *vs.* $1/[\mathrm{M}]$ are curved, and S/I only approximates to $p_{\frac{1}{2}}$. Within a limited pressure range the curvature is small, however, and HL plots can for many practical purposes be treated as linear.[7] Thus, at a given temperature, the straight lines in Figure 2 have been drawn with the same S/I ratio, and this feature is helpful in assessing the points for weakly-intercepting additives (trifluoroethylene and isobutane in particular). The rate–constant ratios derived from these plots are given in Table 1.

The data do not define the parameters in (8) as well as could be hoped, but the overall picture is reasonably consistent and supports the mechanism postulated. The scatter on some of the plots can be traced to the fact that when the additive is not very reactive towards the carbene (*e.g.* trifluoroethylene at 443—462 K or butene at 591—623 K), the ratio $(1 - x)/x$ is very sensitive to errors in the determination of x. The somewhat subjective lines drawn in Figure 2 give more weight to runs which have no inert gas present and with reactant ratios which reduce the above source of error.

TABLE 1

Summary of rate-constants

Temp./K	$(k_2^{\infty}/k^{\circ}_2)$/mol dm^{-3}	Additive	k_3/k_2^{∞}/dm^3 mol^{-1}
ca. 440	0.0022	$\mathrm{Me_3SiH}$ (442 K)	5 700
		$\mathrm{C_3H_6}$ (438 K)	2 700
		$\mathrm{C_2HF_3}$ (432 K)	(45)
		i-$\mathrm{C_4H_{10}}$ (444 K)	(70)
462	0.0025	$\mathrm{Me_3SiH}$	2 800
		$\mathrm{C_3H_6}$	1 400
		$\mathrm{C_2HF_3}$	(65)
		i-$\mathrm{C_4H_{10}}$	(50)
591	0.0035	*cis*-$\mathrm{C_4H_8}$	125
623	0.0045	*cis*-$\mathrm{C_4H_8}$	75

The k_2^{∞}/k_2^{0} values correspond in HL theory to $p_{\frac{1}{2}}$ values of 60, 72, 129, and 175 mmHg respectively, which are similar to those for the unimolecular isomerisation of methyl isocyanide,[8] a molecule with the same number of atoms as trifluoroethylidene. They also give a reasonable Arrhenius plot, with an activation energy difference of $E_2^{\infty} - E_2^{0} \approx 8$ kJ mol^{-1}. In Kassel theory this quantity is given by $(s - \frac{3}{2})RT$, and the value of $s_{\mathrm{eff.}}$ is thus about $3\frac{1}{2}$, perhaps a little lower than expected for a molecule with 12 internal degrees of freedom, but not unreasonably so. The s value required to fit the shape of the fall-off curves for $\mathrm{CH_3NC}$ is *ca.* $2\frac{1}{2}$,[8] although the same value would not necessarily fit the variation of $p_{\frac{1}{2}}$ with temperature.[9]

The temperature variation of k_3/k_2^{∞} (Table 1) allows Arrhenius parameters to be deduced for the various addition and insertion reactions relative to those for the isomerisation process; the results are shown in Table 2. The rate constants for trifluoroethylene and isobutane are too ill-defined to permit this treatment, but the others, although derived from data in short temperature ranges, provide a reasonably consistent picture. An upper limit to A_3 can be obtained as the collision rate constant, *ca.* $10^{11.4}$ dm^3 mol^{-1} s^{-1} for the systems involved, and this sets a *lower limit* to A_2^{∞} of $10^{13.4}$ s^{-1} (propene and butene results) or $10^{14.5}$ s^{-1} (trimethylsilane results). The former value is reinforced by the expected close agreement between the propene and butene results from very different temperature ranges (see Discussion). In addition, the isomerisation of the carbene involves a tight 3-centre complex as shown in (9). Carbene formation reactions, *e.g.* (10), have been found to have normal A-factors (*ca.* $10^{13.5}$ s^{-1}) [2,3,10] in agreement with theoretical predictions.[11] The A-factor for (9) should be similar; the change of the C–C bond to $\mathrm{C}\underline{\cdots}\mathrm{C}$ instead of C ··· C will reduce the entropy of activation by *ca.* 3.4 J K^{-1} mol^{-1}, but this will be offset by the smaller opportunity for loss of rotational entropy in (9). It thus appears that $10^{13.4}$ s^{-1} is a reasonable value for A_2^{∞}, and that the A_3 do indeed approximate to the collision rate constants. The lower limit of $10^{14.5}$ s^{-1} for A_2^{∞} from the trimethylsilane results is improbably high, and is probably in error due to

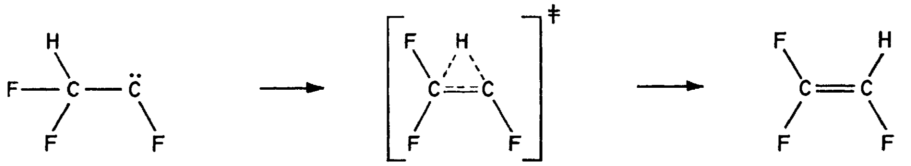
TABLE 2

Relative Arrhenius parameters

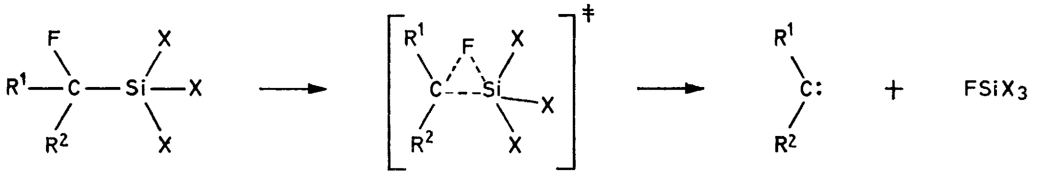
Additive	$(E_2^{\infty} - E_3)$/kJ mol^{-1}	$\log_{10}(A_2^{\infty}/A_3$ mol dm$^{-3})$	E_3/kJ mol^{-1} [c]
$\mathrm{C_3H_6}$	47 [a]	2.1 [a]	49
$\mathrm{C_4H_8}$	46 [a]	1.9 [a]	50
	58 [a]	3.1 [a]	38
$\mathrm{Me_3SiH}$	(49) [b]	(2.0) [b]	47

[a] Experimental values from two-point Arrhenius plots. [b] Preferred values; see text. [c] Assuming $E_2^{\infty} = 96$ kJ mol ^{1}; see text.

the small temperature range involved; if A_2^∞ and A_3 are taken as $10^{13.4}$ s^{-1} and $10^{11.4}$ dm^3 mol^{-1} s^{-1} respectively, and $(E_2^\infty - E_3)$ reduced correspondingly to 49 kJ mol^{-1} (the 'preferred values' in Table 2), the rate constants fit the experimental data with little error.



(9)



(10)

There is not enough information in the experimental data alone to provide unambiguous Arrhenius parameters for the carbene isomerisation (A_2^∞ and E_2^∞). We do, however, have fall-off data, in the form of arbitrarily scaled rate-constants *vs.* pressure, and we can check the data at different temperatures for self-consistency, and obtain information on compatible A_2^∞ and E_2^∞ values, by applying a reliable theory of unimolecular reaction rates. The Forst[12] approximation to $k_{2c}(E)$ in the RRKM theory[6,13] was used to predict fall-off curves for isomerisation of the carbene for a range of values of A_2^∞ and E_2^∞. The vibrational–rotational model of the carbene was constructed from known data for related species (see Appendix). The calculation of the fall-off curves and their use to deduce A_2^∞ and E_2^∞ combinations compatible with the observed HL S/I values (Table 1) are outlined in the Appendix, and the results are quoted in Table 3.

It will be seen that the results for the different temperatures agree reasonably well with one another, thus supporting our interpretation of the experimental data. The spread of activation energies corresponding to any given A-factor gives rise to an uncertainty of up to ±4 kJ mol^{-1}; no doubt greater consistency could have been obtained by adjusting the S/I values within the limits set by the experimental data, but we chose to regard these values as fixed by our original judgment. A greater error is, in fact, introduced by uncertainty in the A-factor, and a reasonable allowance of ±0.4 in $\log_{10}(A_2^\infty/\text{s}^{-1})$ corresponds to an uncertainly of *ca.* 12 kJ mol^{-1} in E_2^∞. There are also uncertainties in the model used for the theoretical calculations, which might reasonably introduce errors of a few kJ mol^{-1} (see the Appendix).

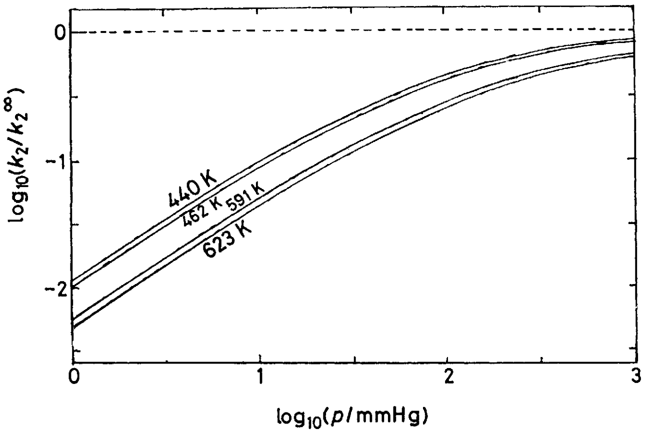


FIGURE 3 Computed unimolecular fall-off curves for the isomerisation of 1,2,2-trifluoroethylidene assuming $A_2^\infty = 10^{13.4}$ s^{-1} and $E_2^\infty = 96$ kJ mol^{-1}

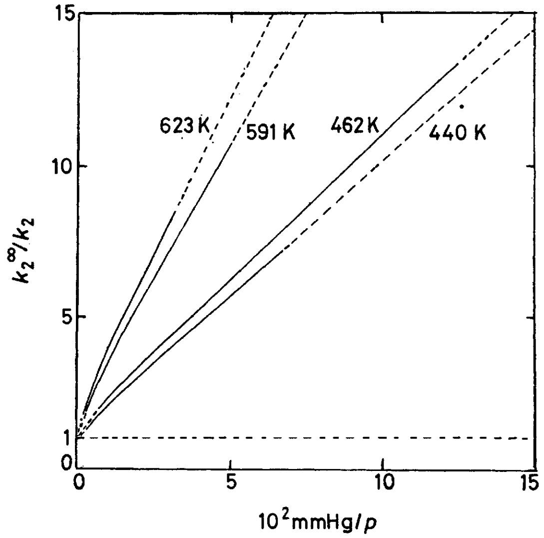


FIGURE 4 Hinshelwood–Lindemann plots corresponding to Figure 3; the unbroken lines indicate the experimental pressure ranges (*cf.* Figure 2)

Thus with the assumption, as discussed above, that $A_2^\infty = 10^{13.4}$ s^{-1} we can derive $E_2^\infty = 96$ kJ mol^{-1}, with a combined uncertainty which is unlikely to exceed ±15 kJ mol^{-1}. The fall-off curves and HL plots corresponding to these parameters are shown in Figures 3 and 4. The HL plots are visibly curved, and this feature could probably be

TABLE 3

Results of RRKM (Forst) calculations

$\log_{10}(A_2^\infty/\text{s}^{-1})$	E_2^∞/kJ mol^{-1} to fit observed S/I at:			
	440 K	462 K	591 K	623 K
12.0	57.6	55.6	54.1	53.0
13.0	87.0	83.8	82.3	80.1
13.4	98.9	96.1	94.2	92.8
14.0	121.7	118.0	115.7	114.2

exploited to assist the model-fitting if sufficiently accurate experimental data were available. Because of the curvature, the S/I values differ markedly from the $p_{\frac{1}{2}}$ values, which are, from Figure 3, 125, 138, 338, and 429 mmHg compared with $S/I = 72$, 72, 117, and 150 mmHg from the HL plots in the experimental pressure ranges at 440, 462, 591, and 623 K respectively. Finally, using $E_2^{\infty} = 96$ kJ mol^{-1}, the activation energies E_3 for the other carbene reactions are calculated from the $(E_2^{\infty} - E_3)$ values as *ca.* 47—50 kJ mol^{-1} (Table 2).

DISCUSSION

There have been very few experimental measurements of absolute Arrhenius parameters for the isomerisation, addition, or insertion reactions of carbenes. Comparative rate measurements, in which a carbene reacts with two competing substrates, have often been carried out only at single temperatures,[14] and even where they cover a temperature range, lead to relative rather than absolute parameters. The systems studied in the present work are also competitive, but have the key feature that the competing reaction is a unimolecular process in its fall-off region. Since the theory of unimolecular reactions is sufficiently established to permit reliable predictions of fall-off behaviour,[6,10,13] and since this behaviour is sensitive to the Arrhenius parameters of the unimolecular process, an additional constraint is imposed upon possible values of the Arrhenius parameters. If one further datum is available, such as a single rate constant for one of the reactions [7] or (as in the present case) an estimated A-factor for the unimolecular reaction, the whole set of parameters becomes determinate. This type of treatment promises to be very valuable in the evaluation of a wide range of reaction systems involving reactive intermediates, particularly in view of the ready availability of computer programs for the unimolecular rate theory calculations.

Returning now to the literature on carbene reactions, relative Arrhenius parameters are available for a few systems, and these allow limits to be placed on some absolute values. The most extensive and reliable data refer to the gas-phase addition of CF_2 to a series of olefins, for which the maximum activation-energy difference of 22 kJ mol^{-1} was found between propene and 2,3-dimethylbut-2-ene.[15] Thus the activation energy for addition of CF_2 to propene must be at least 22 kJ mol^{-1}; it is not possible to estimate how much higher than this limit the actual value might be. The activation energy for addition of CF_2 to tetrafluoroethylene is reported to be 28 kJ mol^{-1}.[16] Data [17,18] for CCl_2 show a maximum activation-energy difference of 7 kJ mol^{-1} between but-1-ene and 2-methoxypropene,[17] but this figure is of doubtful reliability, having been obtained from solution experiments at 0 °C and −78 °C. Data [19] for ^{3}H-fluorocarbene (CTF) refer only to ethylene and *trans*-but-2-ene, with a difference of 3 kJ mol^{-1}. For singlet methylene itself, the clearest indications come from its insertion reactions with dimethylsilane, which proceed at *ca.* 1/50 of the collision rate.[20] This sets an upper limit of 10 kJ mol^{-1} to the activation energy. The independence of the Si–H/C–H insertion ratio on temperature and on the methylene internal energy indicates zero difference in the activation energies of the two processes, suggesting that both may be close to zero. Wave mechanical calculations for addition of singlet methylene to ethylene and insertion into methane indicate virtually zero activation energies.[21] Incidentally, the activation energy for addition of *triplet* methylene to but-2-ene appears to be considerably higher, *ca.* 30 kJ mol^{-1}.[22]

The above data are consistent with the well-known tendency for halogen substitution at a carbene centre to increase the selectivity of the carbene to both addition and insertion reactions.[14] These effects can be correlated semiquantitatively with the inductive and resonance parameters of the substituents; [23] for example, selectivity increases in the series $MeCCl < CCl_2 < CFCl < CF_2$, the selectivity indices m_{XY} being 0.50, 1.00, 1.28, and 1.48 respectively and being predicted with reasonable accuracy by equation (11), where $m_{X,Y}$ is defined as the slope of a plot of $\log(k_{\text{olefin}}/k_{\text{isobutene}})_{CXY}$ *vs.* $\log(k_{\text{olefin}}/k_{\text{isobutene}})_{CCl_2}$ for a series of olefins.[23]

$$m_{X,Y} = 0.53 \sum_{X,Y} \sigma_I - 1.10 \sum_{X,Y} \sigma_R^{+} - 0.31 \quad (11)$$

The increasing selectivity is attributed to decreasing reactivity and increasing activation energy along the series, arising from increasing stabilisation of the carbene by delocalisation of the lone-electron pair. The magnitude of such stabilisation is indicated by the absence of chemically activated isomerisation of the cyclopropanes formed by addition of CTF to olefins in the gas phase; a stabilisation energy of at least 105 kJ mol^{-1} relative to CH_2 has been deduced.[19] Similarly, chemically activated secondary reactions have not been observed in gas-phase additions of CF_2 or 1,2,2-trifluoroethylidene, but they have with CCl_2.[24]

In the light of these observations, the present activation energies of 47—50 kJ mol^{-1} for the addition and insertion reactions of 1,2,2-trifluoroethylidene (TFE) seem very reasonable, since the reactivity of TFE should be similar to those of CFCl and CF_2, for which relatively high activation energies are indicated. Our data do not at present permit a detailed discussion of the selectivity of TFE, but are consistent with a small activation-energy difference for addition to propene compared with *cis*-but-2-ene, comparable with the differences of 6 and 4 kJ mol^{-1} reported for addition of CF_2 [15] and CCl_2 [17] respectively to these two olefins. The rate constants for addition of TFE to propene at 438—462 K and to *cis*-but-2-ene at 591—623 K lie close to the same Arrhenius plot, despite the large difference in observed product ratios (15—50 and 45—95% trifluoroethylene respectively). This is good evidence for the internal consistency of our results from two different systems, and correlates well with extrapolations of the relative addition rates of CF_2 to the same olefins, from 3.6—2.5 in the experimental temperature range 309—

364 K,[15] to 1.8—1.1 in the range 440—623 K of the present results.

It is curious that the activation energy for insertion of TFE into the Si–H bond in trimethylsilane should be so similar to those for its addition to olefins. A conceivable interpretation would be that they are all close to zero, but this does not seem tenable in view of the correlations of structure and reactivity discussed above. More particularly, it would require E_2^{∞} to be *ca.* 48 kJ mol^{-1}, and A_2^{∞} would then have to be *ca.* $10^{11.7}$ s^{-1} to fit the fall-off data; such a value seems unrealistically low. It is also noteworthy that the activation energies for insertion of CF_2 and fluorinated ethylidenes into hydrogen halides are of the order of 40—50 kJ mol^{-1}.[25] The markedly lower rates of reaction of TFE with trifluoroethylene and isobutane can be interpreted in terms of activation energies which are higher by *ca.* 15 kJ mol^{-1} than those for the other reactions, but further work is needed to define such parameters more precisely.

The activation energy of 96 kJ mol^{-1} for the isomerisation of TFE to trifluoroethylene is fairly high for a radical reaction, and is the main factor responsible for the previously noted [3,4] tendency of TFE to add to or insert into substrates rather than isomerise. In contrast, ethylidene,[26] and 2-chloroethylidene and ethenylidene [27] tend preferentially to isomerise, and wave-mechanical calculations suggest that the energy barrier to isomerisation is close to zero for such carbenes.[28] Isomerisation can be regarded as intramolecular insertion of the carbene into its own C–H bond, and stabilisation of the carbene centre by appropriate substitution will, therefore, reduce the rate of isomerisation as well as the rates of insertion. In fact, the isomerisation has a considerably higher activation energy than the addition/insertion reactions, and this accounts for the marked variation in the product ratios with temperature, as noted above.

The present studies have thus revealed the major mechanistic features governing the behaviour of reaction systems involving 1,1,2-trifluoroethylidene. With this understanding it will now be possible to undertake more detailed work to provide extensive quantitative rate and reactivity parameters for the isomerisation, addition and insertion reactions of this and other related carbenes.

APPENDIX

RRKM (*Forst*) *Calculations*.—The vibrational–rotational model for trifluoroethylidene was based mainly on published data for 1,1-difluoroethane [29,30] and difluorocarbene.[31,32] The vibrational wavenumbers are shown in Table 4. The moment of inertia of the CHF_2 group was calculated using the geometry of CHF_2 in $CHF_2\cdot CH_3$,[29] and that of the C–F rotation about the C–C bond using the C–F bond length (130 pm) and F–C–F angle (105°) in CF_2.[30] The reduced moment of inertia was 31×10^{-47} kg m^2.

Fall-off curves were calculated by an ALGOL program on a CDC 7600 computer, using the RRKM theory [6,13] with Forst's approximation to $k(E)$.[12] These lead to equation (12) for the rate-constant as a function of pressure (the nomenclature being that of ref. 6). The state densities $N(E)$ were obtained by the method of steepest descents as formulated by Hoare and Ruijgrok.[34] Integrations for most cases were taken to 40 kcal mol^{-1} above the critical

$$\frac{k_{\text{uni}}}{k_{\infty}} = \frac{1}{Q_2}\int_{E^+=0}^{\infty} \frac{N(E^+)\exp(-E^+/kT)\mathrm{d}E^+}{1 + [N(E^+)/N(E^*)](A_{\infty}/Zp)} \qquad (12)$$

energy in steps of 0.25 kcal mol^{-1} (kcal = 4.184 kJ). In calculating Z, a collision diameter of 0.5 nm and a reduced molar mass of 56.3 g mol^{-1} were used.

TABLE 4

Vibrational data

Vibration in $CHF_2\cdot CF\colon$	Model	Wave-number/ cm^{-1}
2 C–F stretches at CHF_2	as in $CHF_2\cdot CH_3$	1 143, 1 169
C–H stretch	normal value	3 000
C–F stretch at $\ddot{C}$–F	as in CF_2 [a]	1 167
C–C stretch	as in $CHF_2\cdot CH_3$ [a]	1 129
C–$\ddot{C}$–F bend	F–$\ddot{C}$–F bend in CF_2 [a]	668
3 CHF_2 deformations	as in $CHF_2\cdot CH_3$	571, 868, 930
2 CHF_2 rocks		383, 470

[a] The C–F stretches in CF_2 (1 112, 1 224; geometric mean 1 167) [32] are very similar to those in $CHF_2\cdot CH_3$ (1 143, 1 169),[30] (*cf.* also Benson's [33] generalised value of 1 100). We therefore assume that the C–C stretch in $CHF_2\cdot CF\colon$ will be similar to that in $CHF_2\cdot CH_3$, and the C–C–F bend similar to the F–C–F in CF_2.

The resulting values of k *vs.* p were then subjected to HL plots, which were approximately linear, and the least-squares lines, fitted by a Hewlett–Packard 9810A programmable calculator, were used to obtain the S/I values for each A_2^{∞},E_2^{∞} pair and each temperature used in the RRKM calculations. Interpolation on a plot of S/I against log A_2^{∞} at each E_2^{∞} and each T then gave (A_2^{∞},E_2^{∞}) values fitting the observed S/I, as quoted in Table 3. In practice, since A^{∞} and p appear only as their *ratio* in the Forst approximation [equation (12)], the calculation of $k_{\text{uni}}/k^{\infty}$ *vs.* p for a single value of A^{∞} gives the fall-off curves for *any* A-factor, given the same activation energy and the same model of the reactant molecule, by appropriate scaling of the pressure corresponding to each value of $k_{\text{uni}}/k_{\infty}$. Care is needed in the present application, however, to ensure that the data used refer to the pressure range of the experimental HL plots at the appropriate temperature. For example, the experiments at 591 K refer to the pressure range 20—430 mmHg and give S/I = 0.003 5 mol dm^{-3} = 129 mmHg. With $A_2^{\infty} = 10^{13.0}$ s^{-1} and E_2^{∞} = 100 kJ mol^{-1}, S/I at 591 K and 20—430 mmHg is given by the RRKM calculation as 49.8 mmHg (Table 3). If the HL plot were linear, the A-factor required to give S/I = 129 mmHg would be simply $10^{13.0} \times 129/49.8 = 10^{13.41}$ s^{-1}. In fact, however, this S/I now refers to the pressure range 20 × 129/49.8 to 430 × 129/49.8 mmHg, whereas at 20—430 mmHg, $A_2^{\infty} = 10^{13.41}$ s^{-1} gives S/I = 95.7 mmHg, not 129 mmHg. For the same reasons, S/I is not equal to $p_{\frac{1}{2}}$, which is 108 and 250 mmHg respectively for the two cases giving S/I = 49.8 and 95.7 mmHg.

In order to assess the sensitivity of the derived activation energies to the parameters of the model, calculations were also carried out with modified vibrational–rotational models. The least reliable frequency is probably that for the C–C–F bend, and a fairly drastic lowering of this from 668 to 400

cm^{-1} caused a shift of *ca.* 0.1 units in $\log_{10}p$, resulting in a lowering of the activation energy by only 2 kJ mol^{-1}. Similarly, a 20% increase in the cross-sectional area or efficiency of collisions would decrease E_2^∞ by *ca.* 3 kJ mol^{-1}. We conclude that the activation energy corresponding to a given S/I and A_2^∞ is fixed by the calculations to within 5 kJ mol^{-1}.

We thank Imperial Chemical Industries, Nobel Division, for support.

[7/1086 *Received, 22nd June*, 1977]

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