201. *Fluorinated Cyclopropanes. Part III.** *The Reactions of Methylene with Mono-, 1,1-Di-, and Tri-fluoroethylene.*

By F. Casas, J. A. Kerr, and A. F. Trotman-Dickenson.

The rates of addition of methylene from the photolysis of keten to ethylenes to form cyclopropanes have been shown to decrease regularly with fluorine substitution from ethylene to tetrafluoroethylene. The products formed in the reaction of methylene with mono-, 1,1-di-, and tri-fluoroethylene have been determined over a wide range of pressures. The results are interpreted in terms of initial insertion of methylene in C–H bonds and addition to the double bond. The cyclopropanes are initially formed in an activated state. Their relative rates of isomerization to propenes, involving shift of a hydrogen atom, and deactivation have been measured.

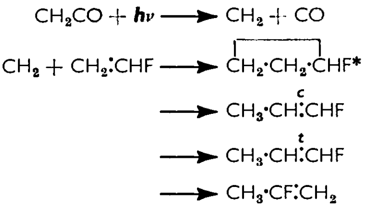
Numerous Papers have described the reactions of methylene with unsaturated hydrocarbons and the isomerization of the activated cyclopropanes formed by the exothermic additions to the double bonds. The thermal isomerizations of some of the cyclopropanes have also been investigated. Such series of related systems provide valuable evidence about the role of energy in unimolecular reactions. An unsaturated hydrocarbon can only be modified by substantial structural changes such as the replacement of a hydrogen atom by a methyl group. This severe alteration must affect many molecular properties; in particular it affects the number of effective oscillators. The substitution of a fluorine for a hydrogen atom does not change the number of atoms in the molecule nor, as the present series of experiments shows, does it introduce new types of reaction; the C–F bond appears to remain unchanged throughout. On the other hand a study of the reaction of methylene with tetrafluoroethylene [1] shows that the activated tetrafluorocyclopropane is about three times as reactive as activated cyclopropane. Unfortunately the products of several of the reactions have not previously been synthesized and their identification therefore presents considerable difficulties. In the present work much reliance is placed on two rules that appear to be generally applicable: first, that methylene does not insert into the C–F bond

* Part II, Casas, Kerr and Trotman-Dickenson, *J.*, 1964, 3655.

[1] Grzybowska, Knox, and Trotman-Dickenson, *J.*, 1963, 746.

to yield $-CH_2F$; second, that C–F bonds are not broken in the isomerization of cyclopropanes containing two or more hydrogen atoms.

Monofluoroethylene.—The photolysis of keten in the presence of monofluoroethylene is expected to follow the path:



$$\mathrm{CH_2CO} + h\nu \longrightarrow \mathrm{CH_2} + \mathrm{CO}$$

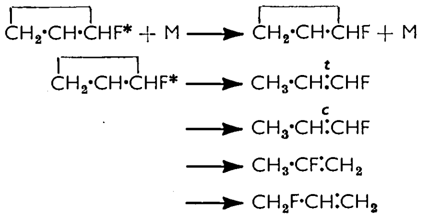
$$\mathrm{CH_2} + \mathrm{CH_2{:}CHF} \longrightarrow \overline{\mathrm{CH_2{\cdot}CH_2{\cdot}CHF}}{}^{*} \qquad (1)$$

$$\longrightarrow \mathrm{CH_3{\cdot}CH\overset{c}{:}CHF} \qquad (2)$$

$$\longrightarrow \mathrm{CH_3{\cdot}CH\overset{t}{:}CHF} \qquad (3)$$

$$\longrightarrow \mathrm{CH_3{\cdot}CF{:}CH_2} \qquad (4)$$

The monofluorocyclopropane formed by reaction (1) contains energy in excess of that necessary for isomerization and will do so, unless stabilized by collision, according to the following equations:



$$\overline{\mathrm{CH_2{\cdot}CH{\cdot}CHF}}{}^{*} + \mathrm{M} \longrightarrow \overline{\mathrm{CH_2{\cdot}CH{\cdot}CHF}} + \mathrm{M} \qquad (5)$$

$$\overline{\mathrm{CH_2{\cdot}CH{\cdot}CHF}}{}^{*} \longrightarrow \mathrm{CH_3{\cdot}CH\overset{t}{:}CHF} \qquad (6)$$

$$\longrightarrow \mathrm{CH_3{\cdot}CH\overset{c}{:}CHF} \qquad (7)$$

$$\longrightarrow \mathrm{CH_3{\cdot}CF{:}CH_2} \qquad (8)$$

$$\longrightarrow \mathrm{CH_2F{\cdot}CH{:}CH_2} \qquad (9)$$

In agreement with this scheme five main products, as shown in Fig. 1, are found at pressures above 50 cm. At lower pressures allene is also formed. It probably comes from the decomposition of activated 2-fluoropropene, as its amount corresponds to the short fall in the yield of the propene. It is possible that the decomposition of propenes also led to the formation of propyne but as its retention time was similar to that of monofluoroethylene it could not be detected.

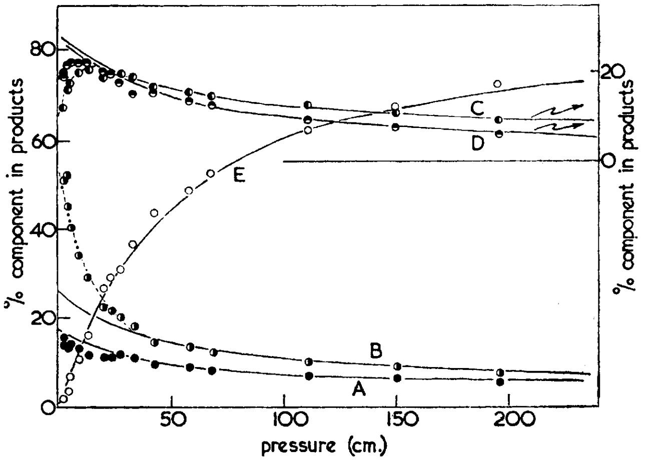


FIG. 1. Variation of yields of products with pressure for the photolysis of keten–monofluoroethylene mixtures (1 : 10). A, 2-Fluoropropene; B and C, *trans*- and *cis*-1-Fluoropropene; D, 3-Fluoropropene; E, Monofluorocyclopropane.

The systematic study of the reaction of methylene was carried out with mixtures containing monofluoroethylene : keten ratios of 10 : 1. A series of runs in which ratio of reactants was varied from 1 : 1 up to 10 : 1, with constant total pressure of 20 cm., showed that the distribution of products varied only a few per cent with the change in the reactants.

At ratios above 6 : 1 there was no variation greater than the experimental error of ±0·3%. Irradiation of similar mixtures for between 20 and 120 min. showed no alteration of product ratios that might be caused by secondary reactions.

By application of standard steady-state treatment to the suggested reaction mechanism, it can be shown that:

$$R(\text{fluorocyclopropane}) = (f_1k_5[\text{M}])/(k_i + k_5[\text{M}]) \text{ and}$$
$$R(\text{fluoropropene X}) = f_x + (k_x/k_5)(R[\text{fluorocyclopropane}]/[\text{M}])$$

where R[fluorocyclopropane] is the % yield of the cyclopropane and R[fluoropropene X] that of a fluoropropene; f_1 is the fraction of reacting methylene that forms cyclopropane by reaction (1) and f_x is the fraction forming fluoropropene by reactions (2), (3), or (4); k_x is the rate constant of one of the isomerization reactions (6)—(9); k_i is the sum of the rate constants of these reactions. According to the first equation a plot of $1/R$(fluorocyclopropane) against 1/[M] should give a straight line with an intercept equal to $1/f_1$ and a slope equal to k_i/f_1k_5. From the second equation, a plot of R(fluoropropene X) against R(fluorocyclopropane)/[M] should also give a straight line with intercept f_x and slope of k_x/k_5. These plots are shown in Figs. 2 and 3 with the total pressure in the system taken for [M].

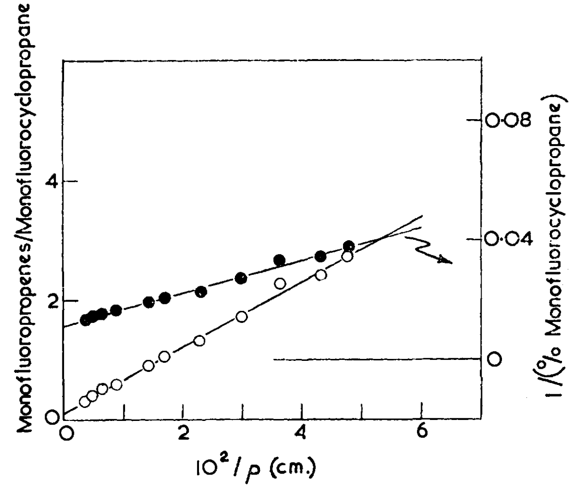


FIG. 2. Linear relations connecting yields of products with pressure in the photolysis of keten–monofluoroethylene mixtures. Right hand scale refers to filled points.

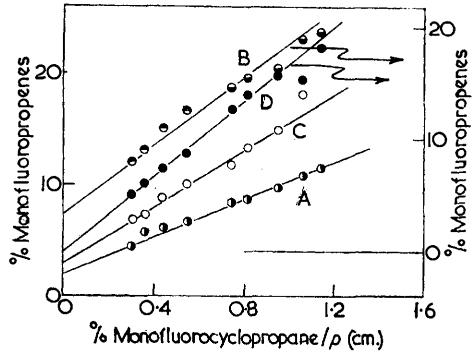


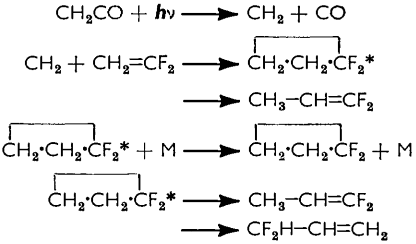
FIG. 3. Linear relations connecting yields of fluoropropenes with yield of monofluorocyclopropane and pressure. A, 2-Fluoropropene; B and C, *trans*- and *cis*-1-Fluoropropene; D, 3-Fluoropropene.

The steady-state treatment also yields the equation:

$$\frac{R(\text{fluoropropenes})}{R(\text{fluorocyclopropane})} = \frac{(k_2 + k_3 + k_4)}{k_1} + \frac{k_i}{k_5[\text{M}]}\left(1 + \frac{k_2 + k_3 + k_4}{k_1}\right)$$

A plot of this linear function is shown in Fig. 2. The construction of these plots involves the identification of the peaks on the chromatogram with the postulated products. On a 6·2 m. column of 30% dibutyl phthalate–firebrick (60—80 mesh) at 0°c flow rate 25 c.c./min. retention times of the peaks were 23 min. (allene); 25 min. (2-fluoropropene); 30 min. (product B); 35 min. (product C); 63 min. (3-fluoropropene); and 71 min. (fluorocyclopropane). The named products were identified by comparison by chromatography and infrared spectra with samples of the known compounds. No other products were formed at high pressures. Products B and C are tentatively identified as *trans*- and *cis*-1-fluoropropene respectively, on the assumption, which seems to hold for many similar pairs of isomers on similar columns, that the *trans*-compound is eluted before the *cis*-. The infrared spectrum is inconclusive.

1,1-*Difluoroethylene*.—The photolysis of keten in the presence of 1,1-difluoroethylene is expected to follow the path:



$$\begin{aligned}
CH_2CO + h\nu &\longrightarrow CH_2 + CO\\
CH_2 + CH_2{=}CF_2 &\longrightarrow CH_2{\cdot}CH_2{\cdot}CF_2^*\\
&\longrightarrow CH_3{-}CH{=}CF_2\\
CH_2{\cdot}CH_2{\cdot}CF_2^* + M &\longrightarrow CH_2{\cdot}CH_2{\cdot}CF_2 + M\\
CH_2{\cdot}CH_2{\cdot}CF_2^* &\longrightarrow CH_3{-}CH{=}CF_2\\
&\longrightarrow CF_2H{-}CH{=}CH_2
\end{aligned}$$

This mechanism is again based on the assumption that methylene does not insert into C–F bonds and that C–F bonds are not broken in the isomerization. Fig. 4 shows that three products are formed. A steady-state treatment similar to that used above yields linear functions of the rates and rate constants which are plotted in Figs. 5 and 6; the agreement is very good.

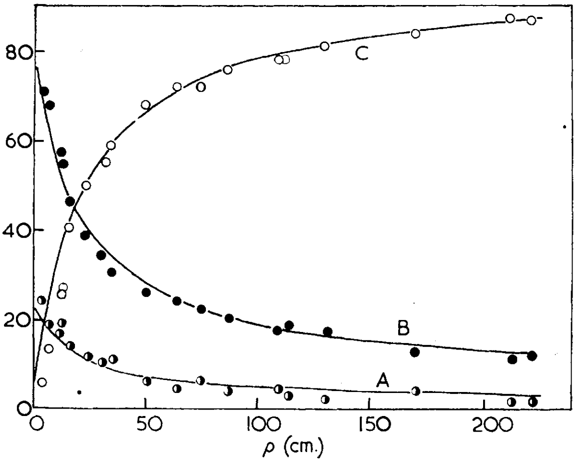


Fig. 4. Variation of yields of products with pressure for the photolysis of keten–1,1-difluoroethylene mixtures (1 : 10). A, 3,3-Difluoropropane; B, 1,1-Difluoropropene; C, 1,1-Difluorocyclopropane.

The identification of the products of this system is reasonably certain. They were eluted from the same column as was used in the monofluoroethylene experiments but with a flow rate of 20 c.c./min.$^{-1}$ at 16, 21·5, and 69 min., respectively. The last peak was the cyclopropane. 1,2-Difluoropropene was the second peak because it is the only difluoropropene that could be formed by insertion of methylene into a C–H bond. The size of the first peak approached zero at high pressures as required by the mechanism. The compound eluted second had a strong infrared absorption at 1730 cm.$^{-1}$ which indicates disubstitution at the double bond. The first compound showed the normal olefinic absorption at 1650 cm.$^{-1}$.

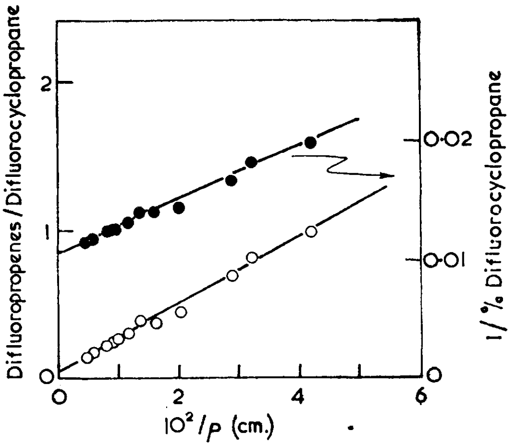


FIG. 5. Linear relations connecting yields of products with pressure in the photolysis of keten–difluoroethylene mixtures.

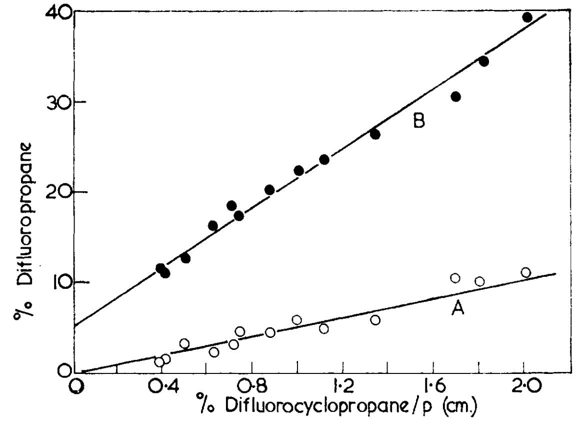
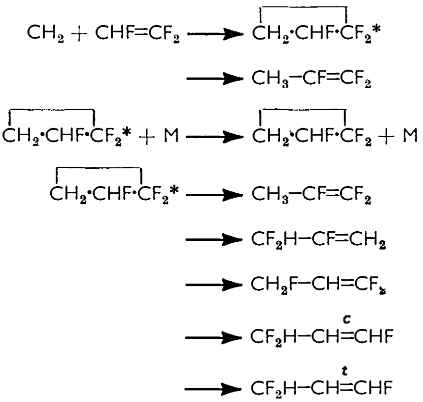


FIG. 6. Linear relations connecting yields of difluoropropenes with yield of 1,1-difluorocyclopropane and pressure. A, 3,3-Difluoropropene; B, 1,1-Difluoropropene.

Trifluoroethylene.—The reaction of methylene with trifluoroethylene is expected to follow the path:



$$CH_2 + CHF{=}CF_2 \longrightarrow CH_2{\cdot}CHF{\cdot}CF_2^*$$
$$\longrightarrow CH_3{-}CF{=}CF_2$$
$$CH_2{\cdot}CHF{\cdot}CF_2^* + M \longrightarrow CH_2{\cdot}CHF{\cdot}CF_2 + M$$
$$CH_2{\cdot}CHF{\cdot}CF_2^* \longrightarrow CH_3{-}CF{=}CF_2$$
$$\longrightarrow CF_2H{-}CF{=}CH_2$$
$$\longrightarrow CH_2F{-}CH{=}CF_2$$
$$\longrightarrow CF_2H{-}CH\overset{c}{=}CHF$$
$$\longrightarrow CF_2H{-}CH\overset{t}{=}CHF$$

It is evident from Fig. 7 that the total number of products agrees with this mechanism as does the formation of only one trifluoropropene at the highest pressures. The rules about the reactivity of the C–F bonds are again confirmed. Steady-state treatment again yields linear relations which can be seen in Figs. 8 and 9 to be well obeyed.

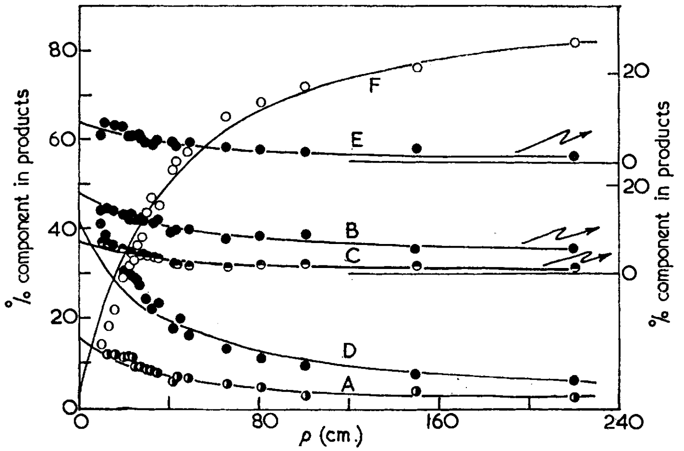


FIG. 7. Variation of yields of products with pressure for the photolysis of keten–trifluoroethylene mixtures (1 : 10). B, 1,1,2-Trifluoropropene; F, 1,1,2-Trifluorocyclopropane. Other trifluoropropenes, lettered in order of elution from the column, not identified.

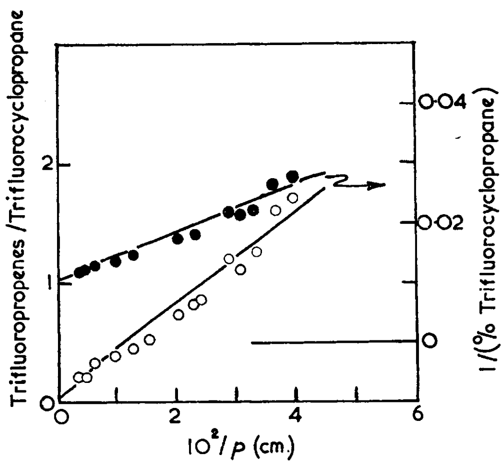


FIG. 8. Linear relations connecting yields of products with pressure in the photolysis of keten–trifluoroethylene mixtures. Right hand scale refers to filled points.

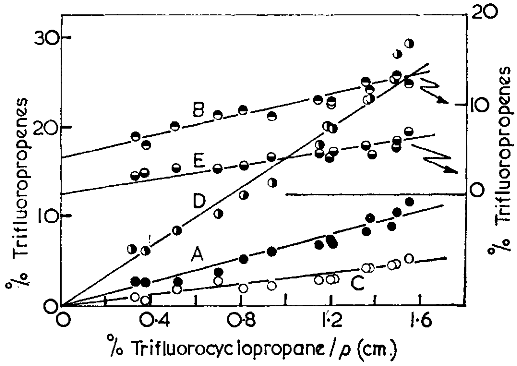


FIG. 9. Linear relations connecting yields of trifluoropropenes with yield of 1,1,2-trifluorocyclopropane and pressure. B, 1,1,2-Trifluoropropene. Other trifluoropropenes, lettered in order of elution from the column, not identified.

Only two products of this reaction system can be satisfactorily identified: trifluorocyclopropane which was eluted from the same column as before at 123 min. with the flow rate at 30 c.c. min.$^{-1}$; and 1,1,2-trifluoropropene, eluted after 22 min., which is the only other product at the highest pressures. Further identification will depend upon the preparation of much larger quantities or the acquisition of authentic samples.

The rate constants derived from the linear plots in the figures are listed in Table 1.

The Reactivity of Ethylenes.—The relative reactivity of the ethylenes was measured in a series of runs at 7 atmospheres total pressure. The ratio of keten : ethylenes was kept at 1 : 10 but the proportions of ethylene to fluoroethylene were varied to compensate for the variations in reactivity so that the amounts of cyclopropanes formed would not vary too greatly. The ethylenes and propenes were absorbed in a mercuric acetate–mercuric

TABLE 1.

Rates of formation of products in the photolysis of keten: fluorinated ethylene (1 : 10) mixtures.

Cyclopropane formed	Monofluoro-cyclopropane	1,1-Difluoro-cyclopropane	1,1,2-Trifluoro-cyclopropane	1,1,2,2-Tetrafluoro-cyclopropane
Fractional yield of products at infinite pressure	Cyclopropane 0·89	0·95	0·97	1·00
	trans-1-F 0·031	1,1-F_2 0·054	1,1,2-F_3 0·040	
	cis-1-F 0·043			
	2-F 0·021			
$10^{10}k$ (sec.$^{-1}$ atm.$^{-1}$) deactivation	1	1	1	1
$10^{9}k$ (sec.$^{-1}$) total isomerization	6·56	2·76	4·88	36·2
$10^{9}k$ (sec.$^{-1}$) Formation of individual fluorinated propenes by isomerization	*trans*-1-F 1·61	1,1-F_2 2·15	A 0·84	1,1,3,3-F_4 36·2
	cis-1-F 1·78	3,3-F_2 0·61	1,1,2-F_3 0·76	
	2-F 1·07		C 0·41	
	3-F 2·18		D 2·14	
			E 0·51	

nitrate mixture[2] before chromatographic analysis. Even at the high pressure, isomerization was not completely suppressed and corrections to infinite pressure were made from the following equation:

$$R(\text{cyclopropane})_{\infty} = \text{A} \times R(\text{cyclopropane})_{\text{exp}}$$

where the constant A has the value 1·147 for ethylene, 1·076 for monofluoroethylene, 1·048 for 1,1-difluoroethylene, 1·061 for trifluoroethylene, and 1·51 for tetrafluoroethylene. Rate constants for addition were then calculated from the typical relation:

$$\frac{k(\text{fluoroethylene})}{k(\text{ethylene})} = \frac{R(\text{fluorocyclopropane})_{\infty}}{R(\text{cyclopropane})_{\infty}} \cdot \frac{[C_2H_4]\text{initial}}{[C_2H_3F]\text{initial}}$$

in this way the relative reactivities were found (Table 2).

TABLE 2.

	Relative reactivity of double bond Exp.	Relative reactivity of double bond Calc.*	Relative reactivity of C–H bond
Ethylene	1	1	0·028
Monofluoroethylene	0·60	0·55	0·019
1,1-Difluoroethylene	0·33	0·31	0·009
Trifluoroethylene	0·16	0·17	0·007
Tetrafluoroethylene	0·10	0·10	—

* Values calculated on the assumption that each successive fluorine substitution reduces the reactivity by a factor of 1·8.

It is seen that the relative reactivities of the double bonds decrease by a factor of 1·8 with the substitution of each successive fluorine atom. This can be explained on the supposition that methylene primarily attacks the π-electrons of a double bond and that substitution with highly electronegative fluorine atoms reduces the π-electron density and hence the reactivity. The attraction of the electrons towards the carbon atoms would be expected to increase the reactivity of the ethylene towards mono-radicals. In agreement with this supposition it has been found that methyl radicals add to tetrafluoroethylene 10 times faster than to ethylene.[3]

Table 1 also shows that the reactivity of the C–H bonds towards insertion is decreased by fluorine substitution. Results with simple olefins have been interpreted as showing that methyl substitution does not affect the reactivity of carbon–carbon double bonds in addition. This deduction is based on the assumption that the rate of insertion of methylene into similar C–H bonds is constant. No direct competitive studies have been made.

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[2] Kerr and Trotman-Dickenson, *Nature*, 1958, **182**, 466.

[3] Szwarc, *Chem. Soc. Special Publ.*, **16**, 106.

The present results indicate that substitution can affect all parts of the molecule and that the assumption of constancy is incorrect. It is therefore possible that the behaviour of methylene with olefins is not so out of line with the behaviour of oxygen atoms and dibromocarbenes as it has seemed.[4]

The Rates of Isomerization of Cyclopropanes.—The rates of isomerization of the fluorinated cyclopropanes listed in Table 2 are based on the assumption that the rate constant for collisional deactivation is constant. This rate constant has been taken as equal to the constant for the rate of collisions of cyclopropane calculated from the simple kinetic theory of gases. It is unlikely that the assumption is strictly accurate, but at the moment there seems to be no better basis for discussion. The corresponding rate constants for the isomerization of cyclopropane, methylcyclopropane, and 1,1-dimethylcyclopropane from the reaction of methylene from keten, ethylene, propene, and isobutene are 1·19, 0·060, and $0{\cdot}0032 \times 10^9$ sec.$^{-1}$, respectively.[5] This monotonous trend can be explained by the increasing number of effective oscillators in the molecules. The other factor that might be important is the relative rates of thermal reaction of the cyclopropanes. At 475° the values of 10^4k (sec.$^{-1}$) are 1·1, 2·8, and 5·7. The increase in the number of effective oscillators is therefore much the most important factor, unless the exothermicity of the additions of the methylene to the three olefins differs by a greater amount than seems possible. The variation in the rates of isomerization of the activated fluoroethylenes must be explained by two competing effects: small increase in the number of effective oscillators in the molecules with increasing substitution offset in the later members of the series by an increase in the reactivity of the cyclopropanes. The second effect can be studied by measurements of the rates of thermal isomerization of the fluorinated cyclopropanes. To obtain information about the first effect one must study the thermal isomerization over a wide range of pressure into the region in which the unimolecular rate constant becomes pressure dependent. The number of effective oscillators can then be found from a Rice–Ramsperger–Kassel treatment. A full interpretation of the results will then depend upon the measurement of the heats of the addition reactions.

EXPERIMENTAL

Keten was prepared by Jenkins'[6] method. Ethylene (Phillips), monofluoroethylene (K and K), and 1,1-difluoroethylene (Matheson) were shown by chromatography to be pure and were simply degassed. Trifluoroethylene was prepared from 1-chloro-2-bromo-1,2,2-trifluoroethane[7] (kindly given by Imperial Chemical Industries Limited) and was purified by gas chromatography. Tetrafluoroethylene was given by Imperial Chemical Industries Limited. 3-Fluoropropene was prepared from allyl bromide and anhydrous potassium fluoride.[8] 2-Fluoropropene was prepared from 1,2-dichloro-2-fluoropropane[9] and purified by gas chromatography.

The reactants in Pyrex bulbs were photolysed with the full light of a medium-pressure mercury arc. Analysis was by gas chromatography with thermal conductivity detector. The sensitivity of the detector to monofluorocyclopropane, 2-fluoropropene, and 3-fluoropropene was found to be the same. It was assumed that its sensitivity did not vary within other sets of isomers.

We thank the British Council for a grant (to F. C.).

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[4] Trotman-Dickenson, " Free Radicals," Methuen, London, 1959, p. 129.

[5] Frey and Kistiakowsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6373; Butler and Kistiakowsky, *ibid.*, 1960, **82**, 759; Knox, Trotman-Dickenson, and Wells, *J.*, 1958, 2897.

[6] Jenkins, *J.*, 1952, 2563.

[7] Henne and Zimmerschied, *J. Amer. Chem. Soc.*, 1947, **69**, 281.

[8] Hoffman, *J. Org. Chem.*, 1949, **14**, 105.

[9] Austin, Coffman, Hoehn, and Raasch, *J. Amer. Chem. Soc.*, 1953, **75**, 4834.