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# 1-Vinyl-1,2,2,3,3-pentafluorocyclopropane: an extraordinarily rapid vinylcyclopropane rearrangement<sup>☆</sup>

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Dedicated to Professor Lev M. Yagupolskii on the occasion of his 80th birthday.

#### Abstract

The synthesis of 1-vinyl-1,2,2,3,3-pentafluorocyclopropane (1) and the kinetics of its thermal, unimolecular rearrangement to 1,4,4,5,5-pentafluorocyclopentene (2) are reported. Kinetic data were obtained by gas-phase <sup>19</sup>F NMR at 80–120 °C, and the activation parameters for the rearrangement of 1 to 2 are:  $\Delta G^{\ddagger}(100 \,^{\circ}\text{C}) = 28.7 \,\text{kcal/mol}$ ,  $\Delta H^{\ddagger} = 26.7 \,\text{kcal/mol}$ , and  $\Delta S^{\ddagger} = -5.5 \,\text{eu}$  (log  $A = 12.7, E_a = 28.4 \,\text{kcal/mol}$ ). Vinyl(pentafluorocyclopropane) (1) with a half-life of only 38 min at 110 °C, is one of the most thermally labile vinylcyclopropanes known. The isomeric *E*- and *Z*-1-propenyl-1,2,2,3,3-pentafluorocyclopropanes (3) similarly have relatively low activation parameters:  $\Delta G^{\ddagger}(E) \cong 28.5 \,\text{kcal/mol}$  and  $\Delta G^{\ddagger}(Z) \cong 31.1 \,\text{kcal/mol}$ . A favorable, polar biradical transition state for rearrangement is proposed to account the exceptional reactivity of these alkenyl pentafluorocyclopropanes.

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Keywords: Vinylcyclopropane rearrangement; Fluorine substitution; Biradical; Gas-phase <sup>19</sup>F NMR; Kinetics

# 1. Introduction

The vinylcyclopropane-cyclopentene rearrangement is an extensively studied, prototypical small hydrocarbon thermal reaction that has characteristics of both stepwise, biradical and concerted mechanisms [1,2]. The kinetics of the parent vinylcyclopropane rearrangement in the gas-phase have been determined by several laboratories, and essentially identical unimolecular Arrhenius parameters have been found: log A = 13.5-13.6 and  $E_a = 49.6-49.7$  kcal/mol [3-5], although somewhat higher values (log A = 14.3,  $E_a = 51.7$  kcal/mol) have been reported more recently [6]. Rate constants and Arrhenius parameters for several substituted vinylcyclopropane rearrangements have been measured [7], including some fluorinated derivatives [8–10]. Gem-difluorination lowers the activation energy for rearrangement by about 8 kcal in 1vinyl-2,2-difluorocyclopropane ( $E_a = 41.5$  kcal/mol) [9,10], and by about 15 kcal/mol in perfluoro(vinylcyclopropane)  $(E_a = 34.6 \text{ kcal/mol})$  [8]. These results are consistent with the well-known effects of fluorination on increasing cyclopropane ring-strain and weakening its C-C bond strengths [11–13]. It might be expected that perfluoro(vinylcyclopropane) would show the largest effect of fluorination whereby the increased cyclopropane ring-strain and decreased C=C  $\pi$ -bond energy work in concert to lower the activation energy. In fact, new partially fluorinated vinylcyclopropanes reported in this paper are notably more thermally labile than perfluoro (vinylcyclopropane) or any other simple substituted vinylcyclopropanes [7].

Gas-phase <sup>19</sup>F NMR has proved to be a convenient, reliable method for determining rate constants and activation parameters for both first- [14–16] and second-order [17] reaction kinetics. In the present work, it is used to determine the kinetics of the rearrangement of 1-vinyl-1,2,2,3,3-pentafluorocyclopropane (1) to 1,4,4,5,5-pentafluorocyclopropane (2), and the isomeric *E*,*Z*-1-propenyl-pentafluorocyclopropane (3) rearrangements to 4 (Scheme 1).

# 2. Experimental

# 2.1. Materials

Solution <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a QE-300 (General Electric, 300 Hz) or a Bruker DRX-400 instrument using tetramethylsilane (TMS) and trichloro-

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4-Bromo-1,1,2-trifluoro-1-butene ( $CF_2=CFCH_2CH_2Br$ ) was obtained from Lancaster Synthesis Inc., and 1chloro-1,2-dibromo-1,2,2-trifluoroethane (BrCF<sub>2</sub>CFClBr) from SynQuest Laboratories Inc., or Fluorochem USA.

# 2.1.1. 2-Bromo-1-(1,2,2,3,3-pentafluorocyclopropyl)ethane(5)

A 11 autoclave was charged with CF<sub>2</sub>=CFCH<sub>2</sub>CH<sub>2</sub>Br (283 g, 1.50 mol) and hexafluoropropylene oxide (415 g, 2.50 mol) and heated at 190 °C for 6 h. After an additional 166 g (1.00 mol) of HFPO was added, the mixture was heated for another 6 h. Crude product (360.5 g) was distilled to give 7.3 g of forecut, bp 87–106 °C, and 329.8 g (92%) of pure **5**, bp 111–112 °C. <sup>19</sup>F NMR:  $\delta$  –152.5 (dt, *J* = 197 (Hz), *J* = 7.2, 2F), –157.1 (dm, *J* = 197, 2H), –212.3 (tt, *J* = 21.5, *J* = 7.1, 1F). <sup>1</sup>H NMR:  $\delta$  3.53 (t, *J* = 7.1, 2H), 2.55 (dm, *J* = 21.5, 2H).

# 2.1.2. 1-Vinyl-1,2,2,3,3-pentafluorocyclopropane (1)

To a stirred solution of KOH (18.0 g) in 15 ml of ethanol and 20 ml of water at 70 °C was slowly added 2-bromo-1-(pentafluorocyclopropyl)ethane **5** (24.0 g, 0.10 mol). During the addition, the volatiles were collected in a -78 °C trap. After the addition was complete, the reaction mixture was stirred at 70 °C for an additional 2 h until no more volatiles were collected. The material collected in the -78 °C trap was distilled to give 9.1 g (58%) of **1**, bp 30 °C. <sup>19</sup>F NMR:  $\delta$  -152.3 (dt, J = 195.4, J = 9.8, 2F), -156.0 (dm, J = 195.6, 2F), -210.7 (t, J = 7.7, 1F). <sup>1</sup>H NMR:  $\delta$  5.86–5.73 (m, 2H), 5.70–5.65 (m, <sup>1</sup>H). IR (gas) (cm<sup>-1</sup>): 3110 (w), 1650 (w), 1515 (m), 1291 (s), 1189 (s), 933 (s). The product **1** is unstable at room temperature and is best stored cold.

# 2.1.3. 2-Chloro-1,4-dibromo-1,1,2-trifluoropentane (6)

A mixture of  $BrCF_2CFClBr$  (749 g, 2.71 mol), benzoyl peroxide (10 g) and propylene (50.0 g, 1.19 mol) was heated

at 80 °C in an autoclave for 8 h and distilled to give 367.4 g of recovered BrCF<sub>2</sub>CFClBr and 367.5 g (97%) of **6**, bp 82–86 °C (25 mm), literature [18] bp 66 °C (11 mm). <sup>19</sup>F NMR:  $\delta$  -62.2 (s), -62.23 (s) (total 2F), -116.8 (m) and -119.7 (m) (total 1F). <sup>1</sup>H NMR:  $\delta$  4.61–4.41 (m, 1H), 3.10–2.56 (m, 2H), 1.87 (m, 3H).

#### 2.1.4. 4-Bromo-1,1,2-trifluoropentene (7)

To a stirred mixture of Zn powder (22.7 g) and 180 ml of i-PrOH at 70 °C was slowly added BrCH<sub>2</sub>CH<sub>2</sub>Br (2.0 g), and the mixture was stirred at 70 °C for 20 min. BrCF<sub>2</sub>CFClCH<sub>2</sub>CHBrCH<sub>3</sub> (6) (95.5 g, 0.30 mol) was then slowly added over 30 min. The resulting reaction mixture was stirred for 6.5 h. All volatiles were distilled and collected in a -78 °C trap at 30 mmHg. The distillate was poured into water and the lower layer was separated, washed with water and distilled to give 41.6 g (90% conversion, 76% vield) of 7, bp 110–114  $^{\circ}$ C and 10.0 g (10%) of recovered starting material. <sup>19</sup>F NMR:  $\delta$  –150.9 (dd, J = 196.5, J = 7.0, 1F, -152.8 (dd, J = 196.5, J = 7.4, 1F) -157.2 (dm, J = 197.6, 1F), -211.2 (m, 1F). <sup>1</sup>H NMR:  $\delta$  4.26 (hext, J = 7.4, 1H), 2.70–2.90 (m, 2H), 1.77 (dd, J = 6.7, J = 0.5, 3H). HRMS: calcd for C<sub>5</sub>H<sub>6</sub>F<sub>3</sub>Br: 201.9605. Found: 201.9622.

#### 2.1.5. 2-Bromo-1-

#### (1,2,2,3,3-pentafluorocyclopropyl)propane (8)

A mixture of **7** (40.0 g, 0.20 mol) and hexafluoropropylene oxide (80.0 g) was heated at 185 °C for 6 h, and then an additional 40 g of HFPO was added and the resulting mixture was heated at 185 °C for another 6 h. After the gas was vented, the residue was distilled to give 40.0 g (80%) of **8**, bp 121–125 °C. NMR indicated a diastereoisomeric mixture. <sup>19</sup>F NMR:  $\delta$  –150.9 (dd, J = 196.5, J = 6.8, 2F), –157.3 (dm, J = 197, 2F), –211.2 (m, 1F) and another isomer:  $\delta$  –152.8 (dd, J = 196.7, J = 7.4, 2F), –157.6 (dt, J = 197.6, J = 7.1, 2F), 211.2 (m, 1F). <sup>1</sup>H NMR:  $\delta$  4.30 (hext, J = 6.8, 1H), 2.51 (m, 2H), 1.81 (d, J = 6.8, 3H). Anal: calcd for C<sub>6</sub>H<sub>5</sub>F<sub>5</sub>Br: H, 2.22; Br, 29.38. Found: H, 2.55; Br, 30.36. HRMS: calcd for C<sub>6</sub>H<sub>6</sub>F<sub>5</sub>Br (–Br): 173.0389. Found: 173.0287.

#### 2.1.6. E,Z-1-(1,2,2,3,3-Pentafluorocyclopropyl) propene (3)

To a stirred solution of KOH (15 g) in 50 ml of ethanol and 50 ml of water at 70–75 °C was slowly added **8** (35.4 g, 0.14 mol), during which volatiles were distilled out and collected in a -78 °C receiver. The distillate was poured into water and the lower layer was separated to give 19.8 g of crude product, which was distilled to give 17.7 g (76%) of pure **3** as a 5:1 mixture of *E*:*Z* isomers <sup>19</sup>F NMR for *E*-**3**:  $\delta$ -152.2 (d, *J* = 194, 2F), -156.3 (dm, *J* = 194, 2F), -202.6(d, *J* = 8.8, 1F); for *Z*-**3**:  $\delta$  -151.9 (dm, *J* = 192, 2F), -157.4 (dm, *J* = 192, 2F), -193 (m, 1F). <sup>1</sup>H NMR for *E*-**3**:  $\delta$  6.28 (dqd, *J* = 15.8, *J* = 6.7, *J* = 2.1, 1H), 5.53 (dm, *J* = 15.8, 1H), 1.88 (m, 3H). *Z*-**3**:  $\delta$  6.38 (m, 1H), 5.44 (m, 1H), 1.86 (m, 3H).





Fig. 2. First-order kinetic plots for 1 to 2 rearrangement.

Fig. 1. Gas-phase <sup>19</sup>F NMR of 1 and 2.

Table 1Rates of thermal isomerization of 1 to 2

Temperature (°C)	80.0	90.0	100.0	110.0	120.0
$k  (h^{-1})$	0.050	0.147	0.400	1.11	3.13
$k \; (\times 10^5 \; \mathrm{s}^{-1})$	$1.39\pm0.01$	$4.08\pm0.04$	$11.1\pm0.1$	$30.8\pm0.3$	$86.9\pm0.9$

# 2.1.7. Rearrangement of E,Z-3: 1,2,2,3,3-pentafluoro-4-methylcyclopentene (4)

A 5-ml tube was charged with **3** (0.23 g, E:Z = 5:1) and then the tube was cooled in liquid N<sub>2</sub> and then evacuated. The content of the tube was stirred at 115 °C for 3.5 h, and then at 131 °C for 1.5 h. NMR analysis indicated a 19.2:1 mixture **4** and unreacted Z-**3**. <sup>19</sup>F NMR (**4**):  $\delta$  –116.1 (dm, J = 239, 1F), –117.8 (dm, J = 255.9, 1F), –122.8 (dd, J = 255.8, J = 14.5, 1F), –127.3 (dm, J = 239, 1F), –139.9 (m, 1F). <sup>1</sup>H NMR:  $\delta$  5.63 (m, 1H), 3.04 (m, 1H), 1.21 (dd, J = 8.3, J = 1.0, 3H). HRMS: calcd for C<sub>6</sub>H<sub>5</sub>F<sub>5</sub>: 172.0311. Found: 172.0324.

# 2.2. Gas-phase <sup>19</sup>F NMR kinetics

The NMR reaction vessel made from a short section of a 10-mm NMR tube, the procedure for loading the tube, and

the automated acquisition of spectra have been described in detail [14,17]. The gas-phase NMR ampules are available commercially from New Era Enterprises, Vineland, NJ. All spectra were obtained with a GE NMR Instruments Omega 360 spectrometer. As before, no field lock is used, and the ampules are not spun.

#### 2.2.1. 1-Vinyl-pentafluorocyclopropane

# (1) – cyclopentene (2) rearrangement

The gas-phase NMR spectrum of **1** at the start of a kinetic run (80 °C) and the spectrum of the rearranged product **2** at the end of the run are shown in Fig. 1. The integrated area of the C–F resonance in **1** at  $\delta$  –212 ppm was monitored with time. Clean first-order kinetics were observed from 80 to 120 °C (Fig. 2), from which the first-order rate constants at 80, 90, 100, 110, and 120 were obtained (Table 1).

Table	2		
Rates	of thermal	isomerization	of E-3 to 4

Temperature (°C) $k (\times 10^4 \text{ s}^{-1})$	90.0 $0.565 \pm 0.01$	$\frac{100.0}{1.44 \pm 0.01}$	$\frac{110.0}{3.58 \pm 0.04}$	$\begin{array}{c} 120.0\\ 9.02\pm0.1\end{array}$
Table 3 Rates of thermal isomerizat	ion of <b>Z-3</b> to <b>4</b>			
Temperature (°C) $k (\times 10^4 \text{ s}^{-1})$	$\frac{110.0}{0.115 \pm 0.01}$	$\frac{120.0}{0.233 \pm 0.02}$	$\begin{array}{c} 130.0 \\ 0.541 \pm 0.05 \end{array}$	$140.0 \\ 1.26 \pm 0.1$



Fig. 3. Eyring plot for 1 to 2 rearrangement.



Fig. 4. Arrhenius plot for 1 to 2 rearrangement.

The activation parameters for the rearrangement and the corresponding 95% confidence limits were obtained by nonleast squares fitting of the Eyring (Fig. 3) and Arrhenius (Fig. 4) equations. For **1** to **2** (Fig. 4),  $\Delta G^{\ddagger}(100 \,^{\circ}\text{C}) = 28.7 \pm 0.1 \,\text{kcal/mol}, \Delta H^{\ddagger} = 26.7 \pm 0.3 \,\text{kcal/mol}, \text{and } \Delta S^{\ddagger} = -5.5 \pm 0.8 \,\text{eu}; \log A = 12.7 \pm 0.05, E_a = 28.4 \pm 0.3 \,\text{kcal/mol}.$ 

# 2.2.2. E,Z-1-Propenyl-pentafluorocyclopropane (3) – cyclopentene (4) rearrangements

The gas-phase <sup>19</sup>F NMR spectra of the starting 5:1 mixture of *E*,*Z*-**3** at 100 °C and the mixture of *E*,*Z*-**3** and rearranged product **4** during a kinetic run (120 °C) are displayed in Figs. 5 and 6, respectively. The C–F resonances in *E*,*Z*-**3** varied slightly with temperature but the integrands of *E*-**3** C–F ( $\delta_{ave} = -203.9$  for 90–120 °C) and *Z*-**3** C–F ( $\delta_{ave} = -198.4$  for 110–140 °C) were easily obtained for the kinetic plots. Good first-order kinetics were obtained (Tables 2 and 3). Least-squares plots of the rate constants

versus temperature gave the activation parameters: (*E*-3 to 4, Fig. 7)  $\Delta G^{\ddagger}(100 \,^{\circ}\text{C}) \cong 28.5 \,\text{kcal/mol}, \Delta H^{\ddagger} = 25.4 \pm 1.7 \,\text{kcal/mol}, \text{ and } \Delta S^{\ddagger} = -8 \pm 4 \,\text{eu}; (Z-3 \text{ to } 4, \text{ Fig. } 8) \,\Delta G^{\ddagger} (100 \,^{\circ}\text{C}) \cong 31.1 \,\text{kcal/mol}, \Delta H^{\ddagger} = 24.5 \pm 4.9 \,\text{kcal/mol}, \text{ and } \Delta S^{\ddagger} = -18 \pm 12 \,\text{eu}.$  The parameters are less precise than those for the rearrangement of 1, particularly for the *Z*-3 isomer.

#### 3. Results and discussion

The three alkenyl pentafluorocyclopropanes for the kinetic studies were easily synthesized from commercially available starting materials using conventional methods (Schemes 2 and 3). The 1-propenyl-pentafluorocyclopropane was prepared as a 5:1 mixture of E,Z-3 isomers, which was not separated but used directly in the gas-phase kinetic runs where the well-resolved methine C–F resonances of the



Fig. 5. Gas-phase <sup>19</sup>F NMR of E,Z-3 (100 °C).



Fig. 6. Gas-phase <sup>19</sup>F NMR of E,Z-3 + 4 (120 °C).



Fig. 7. Eyring plot for E-3 to 4 rearrangement.



Fig. 8. Eyring plot for Z-3 to 4 rearrangement.

isomers ( $\delta_{ave} = -203.9$  and -198.4 ppm) were easily monitored (see Section 2). All three vinylcyclopropanes cleanly rearranged to the expected cyclopentenes and no byproducts were detected by <sup>19</sup>F NMR in any of the kinetic runs. Excellent first-order kinetics were obtained for all three rearrangements, although the data for the slower rearrangement of the minor Z-3 isomer is the least precise. The activation energies for the rearrangements of 1, *E*-3, and Z-3 are compared with those for related vinylcyclopropanes in Table 4.



**3** E:Z = 5:1

 Table 4

 Activation energies for vinylcyclopropane–cyclopentene rearrangements

Vinylcyclopropane	$E_{\rm a}$ (kcal/mol)	Reference
	49.6–49.7, 51.7	[3–5,6]
$H_2$ $H_2$ $H_2$ $H_2$ $H_1$ $H_2$ $H_2$ $H_1$ $H_2$ $H_2$ $H_1$ $H_2$	41.5	[9,10]
	34.6	[8]
$F_2$ $F_2$ $F$ $H$ $H$	$28.4 \pm 0.3, (27.4 \pm 0.3)^{a,b}$	This work
$F_2$ $F_2$ $F$ $H$	$26.2 \pm 1.7^{a,c}$	This work
$F_2$ $F_2$ $F$ $CH_3$	$25.3 \pm 4.9^{a,d}$	This work
<sup>a</sup> Calculated $E_a = \Delta H^{\ddagger}$ - <sup>b</sup> $T_m = 373$ K.	$+RT_{\rm m}$ .	

 $T_{\rm m} = 378$  K.

 $^{\rm d} T_{\rm m} = 398$  K.

The relatively low activation energies for 1 and *E*,*Z*-3, all of which are over 21 kcal/mol less than that for the parent hydrocarbon and even over 8 kcal/mol less than that for the perfluoro(vinylcyclopropane), are truly striking. Vinyl(pentafluorocyclopropane) (1) with a half-life of about 38 min at 110 °C compared with 135 h for perfluoro(vinylcyclopropane) at the same temperature [8], is one of the most thermally labile vinylcyclopropanes known. In fact, we are not aware of any monocyclic vinylcyclopropanes with  $E_a$  or  $\Delta G^{\ddagger}$  values for rearrangement as low as those for 1 and *E*,*Z*-3. A practical consequence of this unusual reactivity is that 1 can be free-radically polymerized with a wide variety of fluorinated monomers to produce copolymers containing the  $-CF_2CF_2CF=CHCH_2$ - repeat unit that is suitable for subsequent grafting or cross-linking [19].

The expected effects of fluorination on cyclopropane ringstrain and its bond strengths alone are clearly not enough to explain the extraordinary reactivity of the alkenyl pentafluorocyclopropanes (see Section 1). A special stabilizing "polar effect" in the transition states, and possibly one favoring transition state-like conformations, that are peculiar to the semi-fluorinated systems with a very electron deficient cyclopropane ring combined with a relatively electron-rich alkene are postulated to explain their unusual kinetic reactivities.



Fig. 9. Polar biradical transition states for rearrangements of alkenyl pentafluorocyclopropanes.

In the conventional biradical transition states for the rearrangements of 1, E-3, and Z-3, there is a favorable, stabilizing polar contribution which is depicted in Fig. 9. Similar polar effects have been invoked to rationalize somewhat related cyclopropylcarbinyl free-radical rearrangements [20,21], although more recent analysis indicates the effect is not important in difluorocyclopropylcarbinyl or difluorooxiranylcarbinyl radicals [22,23]. For the much more electron deficient pentafluorocyclopropyl systems in this study, however, there is greater likelihood that polar effects will be important. Notably, E-3 with its more electron rich double bond compared to that in 1 would be expected to have an even more favorable polar transition state (Fig. 9, E-3ts versus 1ts), and thus should be more reactive than 1. This indeed is the case (Table 4) where  $t_{1/2} = 32 \text{ min at } 110 \degree \text{C}$  for *E*-3 compared with 38 min for 1 at 110 °C. For the Z-3 isomer, however, there is complicating, unfavorable steric repulsion between the syn-CH<sub>3</sub> group and the cyclopropane ring in the transition state Z-3ts that will result in decreased reactivity. In fact, Z-3  $(t_{1/2} = 3.6 \text{ h at } 110 \text{ }^{\circ}\text{C})$  is less reactive than 1 (the uncertainty in the activation parameters for Z-3 makes tenuous any direct comparisons of the data in Table 4, although the comparative rate constants from Tables 1–3 unequivocally show an order of reactivity E-3 > 1 > Z-3).

There is another interesting possible "polar" effect involving a stabilizing charge-transfer interaction between the electron deficient cyclopropane ring and the alkenyl double bond which would favor the syn-conformation approaching the transition state (Fig. 10). Again, the same electronic and steric effects discussed above would favor the syn-E-3 versus syn-1 conformer and relatively disfavor the syn-Z-3 one. Notably, the activation entropies are *negative* for the alkenyl pentafluorocyclopropane rearrangements compared with positive values for the other vinylcyclopropane rearrangements in Table 4 ( $\Delta S^{\ddagger} = -5.5$  eu for 1 versus 2.5 eu for perfluoro(vinylcyclopropane), for example), and likewise their log A values are comparatively smaller  $(\log A = 12.7 \text{ for } \mathbf{1} \text{ versus } 13.5-14.3 \text{ for vinylcyclopropane})$ itself and 13.9 for perfluoro(cyclopropane)). These entropy differences imply more ordered transition states for the alkenyl pentafluorocyclopropane rearrangements, which is consistent with either a "tighter" polar biradical transition state or one involving charge-transfer complexation.

Computational modeling of the alkenyl pentafluorocyclopropane conformations and their transition states for rear-



Fig. 10. Anti and syn conformations of alkenyl pentafluorocyclopropanes.

rangement to cyclopentenes will be needed to better elucidate the electronic effects underlying the observed rate accelerations, but this is beyond the scope of the present work. Despite the lack of a thorough understanding of mechanism and the substituent effects, this work once again demonstrates the dramatic and unexpected effect that fluorine can have on a well-studied, classical small-molecule reaction.

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